#### Memorandum

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December 28, 1995

Place

Department of Pesticide Regulation - 1020 N Street, Room 100
Sacramento, California 95814-5624

Subject RICE PESTICIDE PROGRAM UPDATE

Pursuant to our agreement on how the rice pesticide program would be conducted under a triennial review process, my staff prepared the attached review of the 1995 rice season.

The goal of the program was to meet performance goals for the rice pesticides established by the Board's Basin Plan to protect water quality and prevent toxicity. The five pesticides were the herbicides molinate and thiobencarb and the insecticides carbofuran, methyl parathion, and malathion. The most significant points of this review are:

- Rice acreage decreased from 1994 by four percent; use of the herbicides increased and use of the insecticides decreased.
- Concentrations of the five rice pesticides exceeded performance goals in at least one Sacramento Valley agricultural drain during May and June. Molinate was the only rice pesticide detected in the Sacramento River. Concentrations were less than 0.2 parts per billion.
- The most significant sources of rice pesticides in surface water appear to be aerial drift and seepage beyond the field perimeter.

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- Water holding requirements used to facilitate dissipation of rice pesticides on the site of application appear to be adequate for meeting performance goals.
- Compliance with management practices for minimizing spillage of rice pesticides into surface water was good.
- Flows in agricultural drainage canals were higher than 1994 levels, although water conservation efforts minimize this dilution effect.
- Only eleven variances on water holding requirements
   (emergency releases) were approved; only two releases could
   have contributed to pesticide concentrations at monitoring
   sites.
- Water collected periodically from the Colusa Basin Drain in May and June was acutely toxic to aquatic invertebrates on only one date; pesticides were not a likely explanation for the toxicity.
- Toxicity to aquatic invertebrates of water collected at the discharge point from fields within closed recirculating systems was quickly attenuated downstream within the closed system.

The rice pesticide program for 1996 has the same basic framework as the 1995 program, with the following emphases:

Management practices for containing seepage, and the
pesticides it may contain, will be addressed through
education and implemented through voluntary efforts. Use of
seepage management practices during 1995 will be quantified.

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• Drift control practices call special attention to potential problems associated with aerial applications to properties near agricultural drainage canals and deposition to sweat ditches (small drainage ditches used to channel seepage water away from a field's perimeter).

Please contact me, or have your staff contact Nan Gorder at (916) 324-4265, or Marshall Lee at (916) 324-4269, if you have any questions.

Vand H. Sottell For

James W. Wells

Director

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# Information on Rice Pesticides Submitted to the California Regional Water Quality Control Board Central Valley Region

December 28, 1995

by

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## Department of Pesticide Regulation Information on Rice Pesticides Submitted to the Central Valley Regional Water Quality Control Board December 28, 1995

Programs have been implemented by the Department of Pesticide Regulation (DPR) since 1983 to reduce discharges of the rice herbicides molinate (Ordram®) and thiobenearb (Bolero® and Abolish®) into surface waterways. In 1990, the objectives of these control efforts were clarified and expanded, following the adoption of amendments to the Central Valley Regional Water Quality Control Board's (Regional Board) Water Quality Control Plan (Basin Plan). This plan established performance goals for molinate and thiobenearb beginning in 1990, and for the insecticides carbofuran (Furadan®), methyl parathion, and malathion beginning in 1991.

The following review describes the factors affecting quantities of molinate, thiobencarb, carbofuran, methyl parathion, and malathion discharged to agricultural drains and the Sacramento River and efforts to meet 1995 performance goals. A summary of pertinent water quality monitoring efforts is provided, as well as a memorandum presenting preliminary results from the toxicity study in closed systems. Programs implemented in 1995 helped control discharges of molinate, thiobencarb, carbofuran, methyl parathion, and malathion from rice fields to comply with the performance goals and water quality objective for toxicity in the Basin Plan.

#### **REVIEW OF 1995 PROGRAM**

#### Discussion

A description of the 1995 rice pesticide program is presented in Appendix A. Program requirements were implemented by county agricultural commissioners using restricted material permits. The commissioners also provided information on the voluntary malathion program. A discussion of the aspects of the 1995 program that were different from the 1994 program follows (see Appendix B).

#### Molinate

The 1995 rice pesticide program contained several changes in the required holding periods. The standard molinate holding period remained 28 days in the Sacramento Valley, while the required hold for fields in areas that had historically been granted shorter holding times (water-short areas, in hydrologically isolated fields throughout the rice growing region, and in the San Joaquin Valley) was increased from 8 to 11 days to protect the Regional Board's narrative water quality objective for toxicity.

#### Thiobenearb

The thiobencarb program also retained the basic structure of earlier programs. The standard Bolero holding period remained 30 days in the Sacramento Valley, while the standard Abolish hold was reduced to 19 days. The required hold for fields treated with both formulations of thiobencarb in water short areas and in the San Joaquin Valley was increased from 6 to 19 days to protect the narrative water quality objective for toxicity. Hydrologically isolated fields throughout the rice growing region were required to meet a 6 day hold.

#### Carbofuran, Methyl parathion, and Malathion

The programs for the insecticides retained the basic strategies of the programs used in 1994.

#### Seepage Control

Users of rice pesticides were required to prevent seepage of field water through the field's weir box, generally by securing the box with plastic and with soil to a depth higher than the water level.

Additionally, in 1995, the county agricultural commissioners' offices were supplied with several handouts providing guidance to growers on voluntary seepage prevention measures (see Appendix C). The single page handout was prepared by DPR and numerous interested parties representing the industry, the University of California, the agricultural commissioners, and the United States Department of Agriculture. The handout entitled: Closed Rice Water Management Systems was prepared by the United States Department of Agriculture with the University of California Cooperative Extension. This information was distributed to growers at the time of permit issuance.

#### Use of Selected Pesticides in 1995

In the rice-growing counties in the Sacramento Valley, county agricultural commissioners record the acreage treated with molinate, thiobencarb, carbofuran, and methyl parathion when Notices-of-Application are submitted by the grower to each county office. Based on these records, and on pesticide use reports where available, it was estimated that 332,273 acres were treated with molinate, 106,709 with thiobencarb, 146,216 with carbofuran, and 28,125 with methyl parathion (Table 1). These estimates indicate that molinate use decreased approximately 13.8 percent over use in 1994; thiobencarb use increased 47.0 percent; carbofuran use decreased 1.3 percent; and methyl parathion use decreased 36.7 percent. Pesticide use report data for other important rice pesticides, malathion and bensulfuron methyl (Londax), are not available yet. About

465,000 acres of rice were harvested in California in 1995, a decrease of about 4 percent from the 1994 crop.

#### **Enforcement Activities**

The county agricultural commissioners are responsible for enforcement of the rice pesticide programs. The role of the commissioners and their staffs includes explaining the program to growers, pest control advisers and operators; issuing restricted material permits; inspecting fields for compliance; evaluating emergency release variances; and providing DPR with information on the use of pesticides.

Before any material on the list of California restricted materials may be applied, growers must obtain a permit from their county agricultural commissioner. The permits may specify conditions for use of the material, including post-application water holding requirements. A Notice-of-Intent must be filed with the county agricultural commissioner 24 hours prior to the application, providing the commissioners with the option to observe the mixing, loading, and application of the material, thus enforcing regulations that pertain to pest control operations. Molinate, thiobencarb, carbofuran, and methyl parathion are currently California restricted materials; malathion is not. Permits which specify post-application water holding requirements, like those for the use of molinate, thiobencarb, carbofuran, and methyl parathion, also require that the Notice-Of-Application be filed within 24 hours after the application.

In 1995 DPR and the County Agricultural Commissioners implemented a Prioritization Plan and a Negotiated Workplan. Part of this plan was a negotiated number of waterhold inspections. These plans allow the counties to set priorities within standard guidelines. Rice pesticide applications and water-hold inspections are ranked as "High Priority" inspections as the rice pesticides are restricted materials, and several rice pesticides are under special study by DPR. The county offices then receive partial reimbursement based on numbers of inspections completed.

Staff of county agricultural commissioners and DPR's Pesticide Enforcement Branch inspected 3,163 rice fields for compliance with water holding requirements. They cited seventeen growers for holding violations. Of the seventeen violations, three were in Butte County, ten were in Colusa County, two were in Placer, and two were in San Joaquin County. Only three of the seventeen violations were serious enough to warrant agricultural civil penalty actions. None of the seventeen violations were a result of intential release of water.

Only county agricultural commissioners may grant variances on the holding requirements for fields treated with molinate if the length of the holding time is adversely affecting the rice plants. Growers granted such variances were instructed to drain water only to the

extent necessary to restore a healthy growing environment for the rice seedlings. In 1995, despite unusually cool weather and unseasonable rains, only eleven emergency releases (affecting 772 acres) were issued. In 1994, only three emergency releases, affecting a total of 172 acres, were issued. In 1990 and 1993, when rain in May and June overwhelmed the abilities of growers and irrigation districts to contain irrigation water, emergency releases affected 23,394 and 10,350 acres, respectively (Table 2). In 1991 and 1992, when unseasonable rain did not cause such problems, 2,224 and 1,029 acres, respectively, were discharged under emergency release variances. Clearly, the more restrictive requirements for emergency releases reduced the number of growers qualifying for holding-time variances.

Beginning in 1994, repeat and multiple violators were required, as part of special permit conditions, to make improvements in their water management capabilities. Such improvements may include installation of pumps for tailwater recirculation or leaving land fallow to contain spillage. Growers who violate water holding requirements are subject to maximum penalties within DPR's Enforcement Guidelines. However, conditions preceding violations (e.g., unfavorable field conditions that could not be moderated by the growers' best efforts) may be considered when assessing penalties.

#### Cooperative Water Quality Monitoring Program

DPR had primary responsibility for monitoring in 1995. The primary monitoring site was on the Colusa Basin Drain at Highway 20 in Colusa County. Additionally, the California Rice Industry Association retained the consulting firm Kleinfelder, Inc., to collect water monitoring samples from Butte Slough at Lower Pass Road in Sutter County, and from a site on the Sacramento River at the Village Marina. The chemical analyses of the water samples from all three sites were conducted at the same laboratories. The monitoring protocol is in Appendix D.

Summaries of the monitoring activities addressing molinate, thiobencarb, carbofuran, methyl parathion, and malathion in Sacramento Valley waterways in 1995 are presented below. Locations of monitoring sites referenced in this report are presented in Figure 1.

#### Sampling and Analytical Regimen

Samples were collected twice weekly by DPR at CBD5 from mid-May through mid-July. Samples were collected from Butte Slough and the Sacramento River near the Village Marina by Kleinfelder, Inc., from mid-May to mid-July. During the first and last two weeks of this period, samples were collected weekly, and during the middle six weeks, samples were collected twice weekly.

Samples were delivered to Zeneca Ag Products, manufacturer of Ordram, for molinate analyses. Morse Laboratories of Sacramento performed thiobencarb analyses under contract with Valent, the primary distributor of products containing thiobencarb. Samples were delivered to FMC Corporation, manufacturer of Furadan, for carbofuran analyses and to the California Department of Food and Agriculture (CDFA) laboratory for methyl parathion and malathion analyses. Additional samples representing over half of the total samples collected at CBD5 and analyzed by the primary laboratories were analyzed as quality control samples. Molinate, thiobencarb, and carbofuran concentrations in the quality control samples were determined by the CDFA laboratory, and methyl parathion and malathion by Alta Laboratories. Additional samples were collected and stored; they were analyzed when confirmation of analytical results were required. Blind spikes were periodically submitted for analysis with field samples.

The City of Sacramento analyzed water samples collected from the Sacramento River at the intake to its water treatment plant. Samples were collected on May 17 and twice weekly from May 22 through June 30.

#### Toxicity testing

DPR conducted a toxicity study within Reclamation District 108, a closed system. The objective of the study was to determine whether or not the minimal required holding periods for individual fields within the closed system resulted in toxicity to aquatic invertebrates within the system. A memorandum is attached as Appendix E that describes the study and presents preliminary results.

Water samples were collected from the Colusa Basin Drain at CBD5 weekly from mid-April through late June. Department of Fish and Game staff exposed neonate (<24 hours old) cladocerans (Ceriodaphnia dubia) to sample water for 96 hours, as well as to control water samples. Percent survival was recorded.

#### Results of the 1995 Monitoring Program

Results of the monitoring program are found by monitoring site in Tables 3, 4, and 5.

#### Molinate

The Zeneca laboratory reported the highest concentration of molinate detected in these waterways in 1995 was 25 parts per billion (ppb) at CBD5 on May 25. These data indicate the performance goal for molinate (10 ppb) was exceeded in the Colusa Basin Drain, but not in the Butte Slough or the Sacramento River (Table 6). Table 7 presents the peak concentrations of molinate in Sacramento Valley waterways in each year since 1980.

The highest concentration of molinate detected in the Sacramento River in 1995 was 0.16 ppb in a sample collected by the City of Sacramento at the intake to its water treatment facility on June 22 (Table 6). A peak of 1.7 ppb was found there in 1993. The maximum contaminant level for molinate, established to protect public health, is 20 ppb.

#### Thiobencarb

Analytical results reported by Valent indicated thiobencarb concentrations in the agricultural drains were highest in the Colusa Basin Drain (CBD5), where they peaked at 3.5 ppb on June 8 (Table 3). Based on these results, the thiobencarb performance goal (1.5 ppb) was exceeded on three sampling dates over a two week period in the Colusa Basin Drain, but not in Butte Slough (Table 4) or the Sacramento River (Table 5). Table 8 presents the peak concentrations of thiobencarb in Sacramento Valley waterways in each year since 1980. The City of Sacramento did not detect thiobencarb in the Sacramento River in 1995 (Table 6).

#### Carbofuran

Results of carbofuran analyses performed by FMC are presented in Tables 3, 4, and 5. The performance goal for carbofuran (0.4 ppb) was exceeded in the Colusa Basin Drain at CBD5 on five sampling dates, where a peak concentration of 0.70 ppb was detected. The performance goal was also exceeded in Butte Slough on two occasions. No carbofuran was detected in the Sacramento River. The peak concentration in 1994 was 2.3 ppb at CBD5.

#### Methyl parathion

Results of methyl parathion analyses performed by CDFA indicated that the methyl parathion performance goal (0.13 ppb) was exceeded in Butte Slough on June 1 (Table 4), with a level of 0.187 ppb. This sample had the highest concentration detected in the 1995 program. The performance goal was not exceeded in the Colusa Basin Drain or the Sacramento River. The peak methyl parathion concentration in 1994, 2.1 ppb, was detected in a sample collected from CBD5.

#### Malathion

Analytical results indicated the malathion performance goal (0.1 ppb) was exceeded at CBD5 on May 16 and 18 when 1.033 and 0.345 ppb were detected (Table 3). In 1994, the peak malathion was detected at CBD5, at a concentration of 0.32 ppb.

#### Toxicity testing

DFG staff observed significant toxicity on only one date (see Appendix F), and it was probably not attributable to pesticides as the pesticide concentrations in the split samples were not high enough to explain the toxicity (Fujimura 1995).

#### Quality assurance/control program

All laboratories performed well on internal quality assurance and when provided with blind-spike samples. The detailed Quality Assurance Program is in Appendix G.

Analytical results were available for comparing primary laboratory results with quality control laboratory results within each pesticide. Regression analyses were conducted when quantitative data were available; molinate and thiobencarb were analyzed but the numerous non-detects for carbofuran, methyl parathion, or malathion precluded regression analyses. The assumption that precision does not vary with concentration was made in order to complete the regression analyses. There is no evidence of systematic differences between the analytical results from the primary and quality control laboratories for molinate and thiobencarb. The quality control data are included in the tables listing results of the primary laboratories.

When primary laboratories found unusually high concentrations or the initial samples collected were lost, backup samples were analyzed.

#### Mass Transport of Pesticides in Agricultural Drains and the Sacramento River

Estimates of the total mass of pesticides transported in agricultural drains and the Sacramento River may be used to compare pesticide loading in different years. However, mass transport cannot be used to determine compliance with performance goals. The flow data only recently became available, thus mass transport has yet to be calculated.

#### Weather and Its Influence on Water Quality

Weather conditions, especially those during and after applications of rice pesticides, influence the performance of water quality control programs. Dissipation rates of many pesticides, e.g., molinate, increase with increasing temperature, so warm weather during water holding periods helps reduce concentrations. Warm weather in May of 1987 and 1992 helped explain why concentrations in waterways and mass transport in the Sacramento River were relatively low in those years. Conversely, in May 1990 and in late May and early June 1993, cool and rainy conditions prevailed, and the results of the molinate program were not as successful. Thus, it is important to be aware of weather patterns when reviewing monitoring data.

The 1993 weather pattern was not conducive to pesticide dissipation and the large number of emergency variances on water management requirements resulted in unusually high pesticide loading in the agricultural drains and the Sacramento River. Likewise, the 1995 season was unusually cool and wet, and not conducive to pesticide dissipation.

#### Flows in Agricultural Drainage Canals and the Sacramento River

Freshwater flows dilute pesticide-laden water that may enter surface waterways. With the reprieve from the drought, flows in the Colusa Basin Drain in 1995 increased over 1994. Yet, due to water conservation practices in rice-growing areas of Glenn and Colusa Counties, discharges through the control gates at Knight's Landing were eliminated from May through early June. Butte Creek flows were high and they ran for an extended period compared to recent years. This dilution effect may be a partial explanation for the low pesticide concentrations detected at the Butte Slough monitoring site. Additionally, unseasonable rains may have resulted in increased flows in all waterways intermittently throughout the season.

#### Sources of Pesticides in 1995

Pesticides used in rice culture may enter surface water from five sources under normal conditions. Drift during aerial applications and transport through levees with seepage water can be expected to contribute to loading during and shortly after the application period. Discharges from fields prior to the end of the legal holding times (i.e., illegal releases and emergency releases) are most prevalent two to four weeks following application. Legal releases are the predominant source of loading after the water holding requirements lapse. By examining the occurrence of rice pesticides in surface water in relation to their application schedules (Figures 2-6), presumptions can be made regarding the effects of each potential source.

#### Aerial drift

The 1995 rice pesticide program had specific provisions for reducing the effects of aerial drift on water quality, described above. Evidence suggests that aerial drift may continue to account, in part, for peak concentrations of all the rice chemicals in the Colusa Basin Drain. When peak concentrations occur early in the season, and at irregular intervals, the source is likely drift at the time of application. It is significant to note that flows in the Colusa Basin Drain during the period of peak concentrations were relatively low, as measured by the gauge at SR 20. Thus, the Drain had very little capacity to dilute contamination from aerial drift.

#### Seepage

In some rice fields, field water can move laterally through levees and beyond the perimeter of the field. Often levee borrow pits are used as a conveyance for this water (in this case known as "sweat ditches") and, when seepage flows are high enough, discharge the water into local drainage canals. Molinate, apparently transported with this seepage, has been detected in water in sweat ditches at concentrations as high as 840 ppb, even after the ditches were tarped to eliminate influences of aerial drift (Pino 1992). Staff of the Regional Board sampled four sweat ditches in 1994, although in this survey the ditches were not tarped. Molinate was detected in each ditch at concentrations ranging from 44 to 1300 ppb; carbofuran, from 0.4 to 11 ppb. At one of the sites, molinate granules were visible on both sides of the sweat ditch, apparently the result of an inaccurate aerial application. Such aerial deposition of pesticides to sweat ditches is another means of transporting pesticides offsite into surface waterways.

The seasonal changes in molinate concentrations at CBD5 are more characteristic of sustained inputs like seepage than of the effects of incidental aerial drift, as was seen with methyl parathion and thiobencarb. Concentrations rose shortly after the application season began; this was well before sustained post-application drainage from rice fields could occur.

#### **Emergency releases**

Only twelve emergency releases were granted in 1995, suggesting growers planned carefully for unusual weather patterns. The total area affected was 772 acres. Two emergency releases (114 acres) could potentially have contributed to the peak concentrations of molinate in the Colusa Basin Drain. The locations and dates of the other nine releases did not correspond with detections of pesticides at downstream monitoring sites.

Additionally in 1995, the Natomas Mutual Water District contacted DPR after unusual rains in June to request permission to release water from Reclamation District 1000, a system normally closed at that time of year. The rain water created a risk of levees bursting. After consultation with staff at the Regional Board, DPR agreed to allow pumps to be activated to avoid the potential damage resulting from burst levees. Pumps ran to discharge water from the system on June 17 and 18. DPR staff collected water samples from this discharge for chemical analyses on June 17, 18, an 19. Carbofuran was not detected above the limit of quantitation (0.35 ppb). Molinate and thiobencarb were present on June 18 only at 4.2 and 0.6 ppb, respectively.

#### Illegal releases

A review of monitoring results could not identify any effects these violations may have had to downstream water quality.

#### Legal releases

Evidence suggests that the length of the holding times in the Sacramento Valley is adequate to meet performance goals. After June 15, the approximate date on which the early post-application discharges may resume from treated fields, the presence of pesticides in regional waterways appears to be incidental and not characteristic of the sustained contamination expected from inadequate holding requirements. In most cases, performance goals during this period were not exceeded on two consecutive sampling dates, indicative of sources of contamination that are transitory, such as aerial drift from late season applications or illegal releases.

#### Additional information on thiobencarb

In 1994, the limitations on the sales of thiobencarb products were removed. Programmatic changes such as the berming of drainage structures and shorter required holding times for water treated with Abolish 8EC were thought to be helpful in improving water quality overall and precluded the need for a sales limitation. The liquid formulation of thiobencarb is shown to have a lower potential for off-site movement than Bolero, the granular formulation. Use information indicate thiobencarb use was within the limits defined by earlier sales limitations. In addition, results of the 1994 monitoring do not suggest the increased use of thiobencarb adversely affected water quality.

United Agricultural Products (UAP), distributors of Abolish, submitted data regarding the use of Abolish on fields where the "pin-point flood" method of water management, a method similar to the "Leather's method", is used. Such fields are flooded, then drained or allowed to dry soon after seeding to help promote root growth in the seedling. Abolish is then aerially applied and the field is reflooded. UAP's data show that thiobencarb concentrations are initially higher in field water treated in this manner, compared to fields treated with the "preflood surface" method (Heier and Sakamoto 1994). However, field concentrations appear to decline quickly so that by nineteen days, the last day of the Abolish holding time in most situations, concentrations are about the same as those in fields treated using the "preflood surface" method. It was demonstrated earlier (Valent 1993) that the potential for thiobencarb to be discharged from a field treated with Abolish 8EC using the preflood surface method was much lower than from a field treated with Bolero 10G.

Thiobencarb use increased dramatically in 1995 (up 47 per cent over 1994). This increase can be partially attributed to the usefulness of thiobencarb as a resistance

management tool for weed resistance against Londax. Additionally, with the cool spring weather, many growers used the pin-point flood method of seedling establishment, and Abolish is readily employed in that practice. Thiobencarb concentrations in the agricultural drains in 1995 remained similar to those of recent years despite the increase in use.

#### 1996 PROGRAM

#### **Program Descriptions**

In 1996, the rice pesticide program will continue to use restricted material permits and associated conditions to implement water management practices that reduce pesticide discharges into surface waters. In addition, management of other important sources of contamination will continue to improve. These practices, when fully implemented, are expected to result in attainment of water quality objectives and protect performance goals.

The program description will not differ from that described in the memorandum to the agricultural commissioners in Appendix A.

#### Discussion

#### Study of toxicity in closed irrigation systems

DPR completed the field work on a study of toxicity within closed systems (see Appendix B). The preliminary results show that, generally, water discharged from the fields to the system was not toxic. When water released from the site of application is toxic at the discharge point, this toxicity is quickly attenuated as the water mixes with the larger waters of the closed system. Thus, no changes are proposed for holding times for fields within closed systems, as the narrative water quality objective for toxicity appears to be protected within the system.

#### Water holding requirements

The water holding requirements in the Sacramento Valley in 1995 were adequate to meet performance goals and will not be adjusted in 1996. These holding requirements will continue to prevent acutely toxic discharges as well. To prevent acutely toxic discharges of pesticides in the southern Sacramento and San Joaquin Valleys, water holding requirements for most users of molinate and thiobencarb were increased in 1995 and will not change in 1996. However, water holding times will not be increased in multi-grower closed systems. Rice growers in one of the several hydrologically isolated areas may

request the county agricultural commissioner to evaluate, on a case-by-case basis, the characteristics of the local drainage system to determine whether discharged water has hydrologic continuity with perennial streams.

#### **Drift Control**

Drift control provisions will be as they were in 1995, and special attention will be given to prevent aerial deposition to sweat ditches during application.

#### Seepage

Seepage appears to make significant contributions to the pesticide load in local drainage canals. Molinate and carbofuran have been detected in sweat ditches at concentrations high enough to exceed levels reported to be acutely toxic to aquatic invertebrates by Harrington (1990) and Menconi and Gray (1992). Management practices are available that will help minimize these contributions and will be promoted (as in the 1995 season) as means to minimize pesticide movement with seepage.

DPR will work with county agricultural commissioners, University of California Cooperative Extension, and the Natural Resources Conservation Service (formally the Soil Conservation Service), and the California Rice Industry Association to educate growers on the potential adverse effects of discharged seepage and to promote voluntary implementation of practices that will help minimize these effects.

DPR, along with county agricultural commissioners, will continue its efforts to identify areas where seepage contributes to local water quality problems and will track voluntary efforts taken by growers to contain or reuse seepage water.

#### Emergency releases

No changes in the provisions for emergency releases are considered for 1995.

#### Education

As was the case in 1995, DPR staff will use opportunities to educate growers, pest control advisors, and applicators on the unique problems of rice pesticides and surface water contamination.

### Enforcement

County agricultural commissioners will continue the enforcement program outlined above.

#### Monitoring

DPR will continue to assume the responsibility of planning and implementing the monitoring program in 1996. While the protocol only provides for monitoring one site (the Colusa Basin Drain at CBD5), it does not preclude DPR from sampling additional sites if conditions indicate a need. The City of Sacramento will continue to monitor its water intake on the Sacramento River for the presence of molinate and thiobencarb. DFG will continue to perform toxicity tests using water collected from CBD5.

#### REFERENCES

Fujimura, R. 1995. Memorandum to Brian Finlayson, Department of Fish and Game: Aquatic toxicology laboratory report, results of examination (Aug. 1, 1995). Calif. Dep. of Fish and Game, Pesticide Investigations Unit, Elk Grove.

Harrington, J.M. 1990. Hazard assessment of the rice herbicides molinate and thiobencarb to aquatic organisms in the Sacramento River system. Calif. Dep. of Fish and Game. Environ. Services Div., Admin. Rep. 90-1, Rancho Cordova.

Heier, J.L. and S.S. Sakamoto. 1994. Rice field tailwater monitoring utilizing pin point flood cultural practice. United Agricultural Products.

Menconi, M. and S. Gray. 1992. Hazard assessment of the insecticide carbofuran to aquatic organisms in the Sacramento River system. Calif. Dep. of Fish and Game, Environ. Services Div., Admin. Rep. 92-3, Rancho Cordova.

Schnagl, R. and W. Wyels. 1993. Memorandum to Marshall Lee, Department of Pesticide Regulation: Molinate concentration in rice field discharges, 1993 (Aug. 6, 1993). Calif. Regional Water Qual. Control Board, Central Valley Region, Sacramento.

Valent. 1993. Abolish 8EC rice herbicide: proposal for inclusion into the 1993 rice pesticide control program (Feb. 10, 1993). Valent U.S.A. Corporation, Walnut Creek.

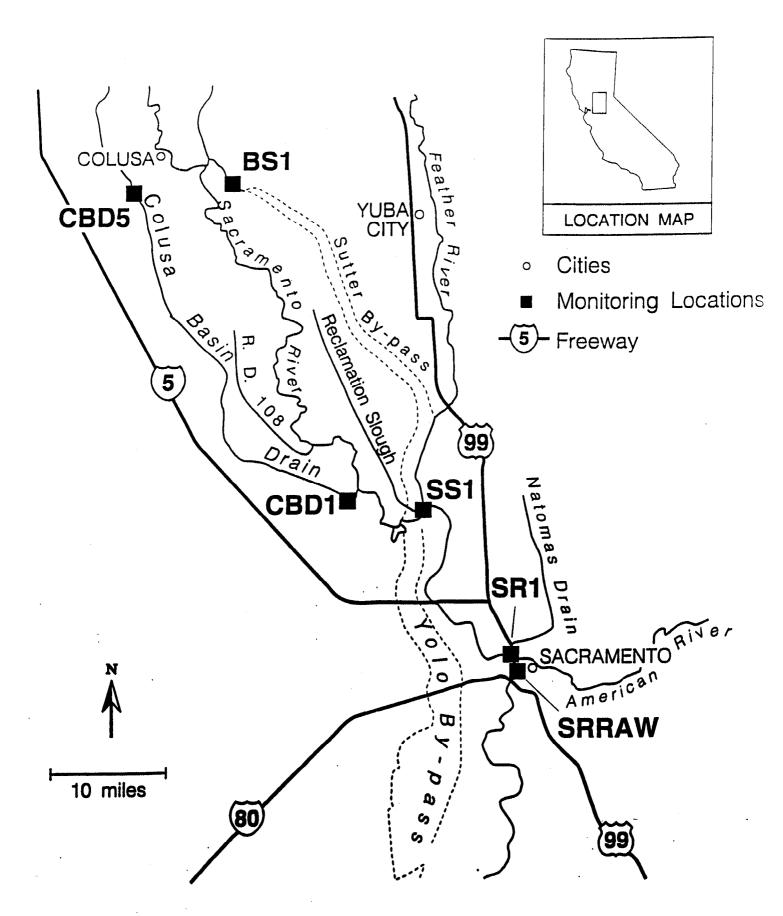


Figure 1. Pesticide monitoring sites in the Sacramento Valley

#### Monitoring sites in the Sacramento Valley

CBD5	Colusa Basin Drain near Highway 20 in Colusa County.
CBD1	Colusa Basin Drain at Roads 109 and 99E near Knight's Landing in Yolo County, near its outfall on the Sacramento River.
BS1	Butte Slough near Highway 20 in Sutter County.
SS1	Sacramento Slough at the Department of Water Resources gauge station in Sutter County, near its outfall on the Sacramento River.
SR1	Sacramento River approximately 1.5 km upstream from the confluence with American River, at the Village Marina in Sacramento County.
SRRAW	Sacramento River at the intake to the water treatment facility in Sacramento, approximately 0.3 km downstream from confluence with American River, in Sacramento County.

Figure 2. Acres treated with molinate in Colusa and Glenn Counties and concentrations of molinate in the Colusa Basin Drain near SR20 in 1995.

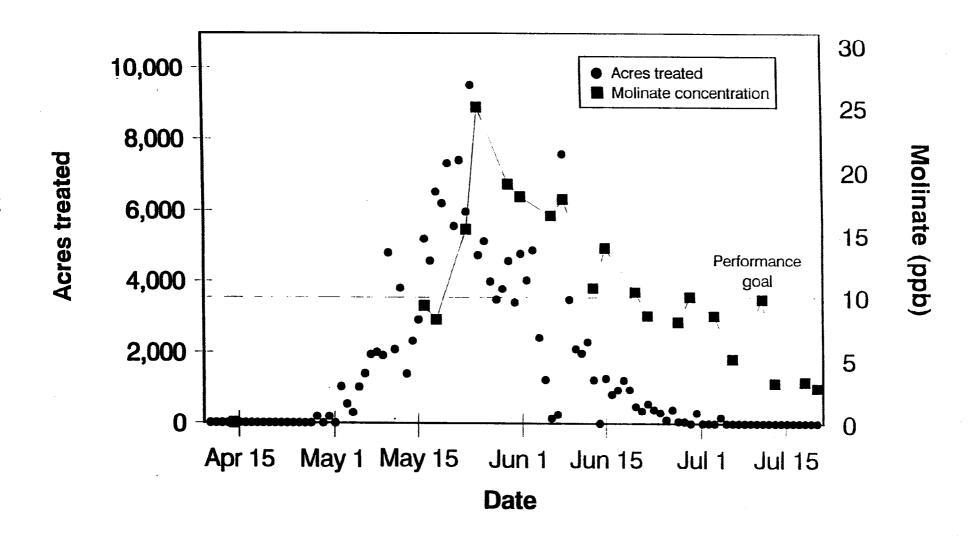


Figure 3. Acres treated with molinate in Butte County and concentrations of molinate in Butte Slough near SR20 in 1995.

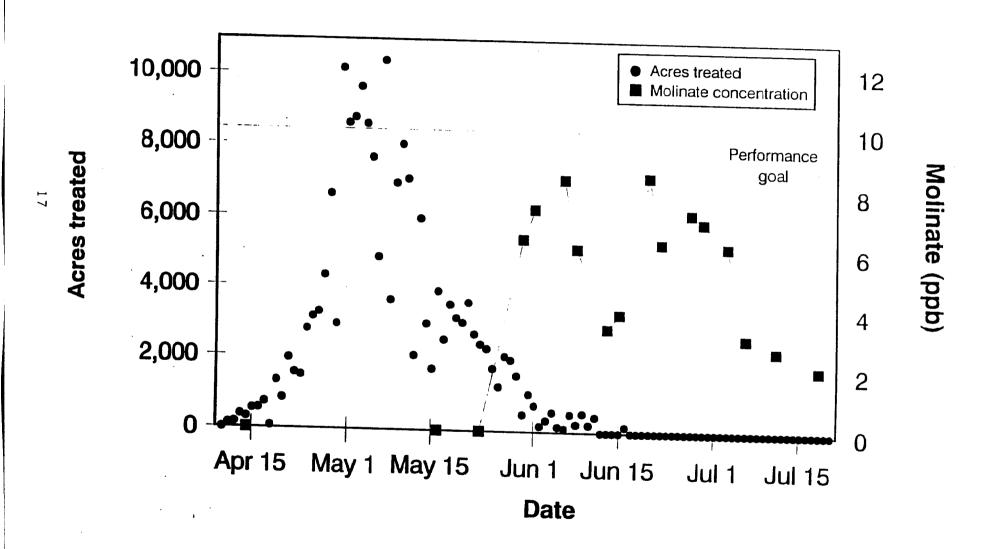


Figure 4. Acres treated with thiobencarb in Colusa and Glenn Counties and concentrations of thiobencarb in the Colusa Basin Drain near SR20 in 1995.

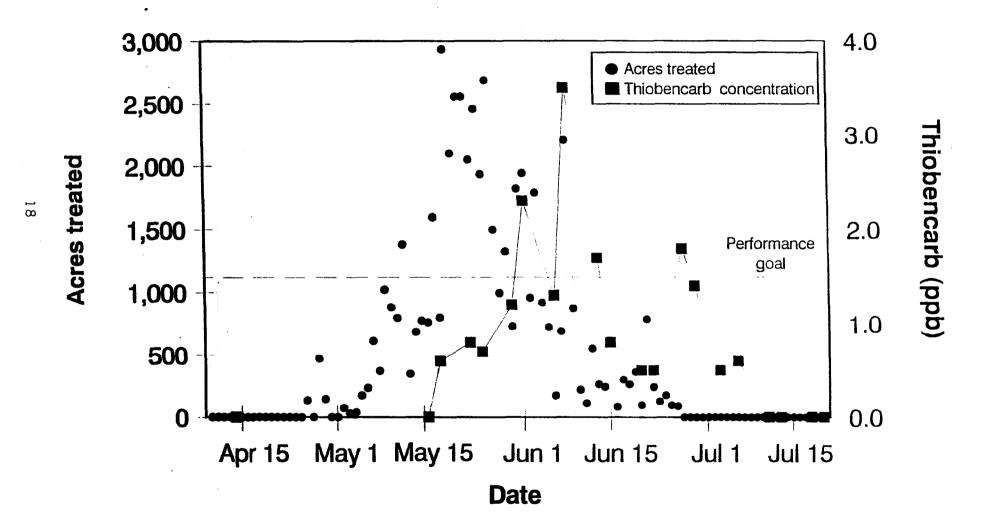


Figure 5. Acres treated with methyl parathion in Colusa and Glenn Counties and concentrations of methyl parathion in the Colusa Basin Drain near SR20 in 1995.

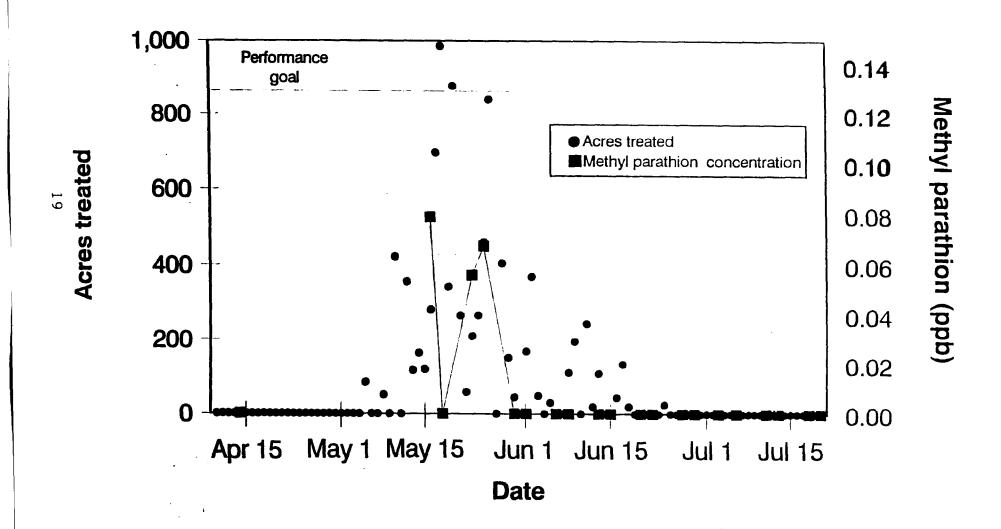
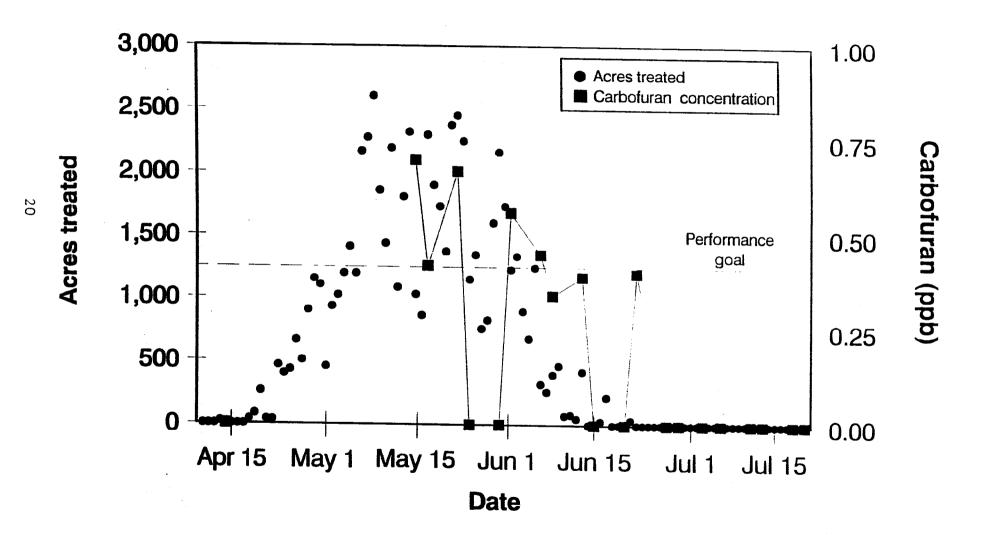


Figure 6. Acres treated with carbofuran in Colusa and Glenn Counties and concentrations of carbofuran in the Colusa Basin Drain near SR20 in 1995.



**Table 1.** Acres treated with molinate (Ordram<sup>2</sup>)<sup>1</sup>, thiobencarb (Bolero<sup>2</sup> and Abolish<sup>2</sup>), carbofuran (Furadan<sup>2</sup>), and methyl parathion in the counties of the Sacramento Valley in 1995<sup>2</sup>.

		Acres treated			
<u>County</u>	<u>molinate</u>	thiobenearb	<u>carbofuran</u>	methyl parathion	
Butte	70.338	9,456	40,261	1,941	
Colusa	88,346	45,171	42.388	7.322	
Glenn	71.381	6,689	21,202	1.393	
Placer	8,540	7,668	6,566	1.194	
Sacramento	6,306	1,493	309	1,344	
Sutter	49,158	24.230	23,777	9.877	
Tehama	1,302	0	147	0	
Yolo	13,651	7,947	350	461	
Yuba	23,251	4,055	11,216	4,593	
Totals	332,273	106,709	146,216	28,125	

- 1. Molinate may be applied more than once at each site.
- 2. Most values are based on Notices-of-Application submitted to county agricultural commissioners.

**Table 2.** Acres of molinate-treated rice fields where water was discharged under emergency release variances in the Sacramento Valley in 1987 - 1995.

		Percent of total
<u>Year</u>	Acres	acres treated
1987	5,712	1.94
1988	4,897	1.41
1989	3,235	0.86
1990	23,394	6.32
1991	2,224	0.70
1992	1,029	0.29
1993	10,350	2.50
1994	172	0.04
1995	772	0.23

Table 3. 1995 Pesticide Concentrations at the Colusa Basin Drain near Highway 20 in Colusa County (CBD5) in parts per billion (ppb)

Samples collected by the Department of Pesticide Regulation unless noted otherwise.

		Molina	te	Thiober	ncarb	Carbofu	ran	Methyl pa	rathion	Malath	ion
Laboratory Reporting limit Date		Primary 1.0		Primary 0.50	QC 0.50	Primary 0.35	<u>QC</u> 0.10	Primary 0.05	<u>QC</u> 0.10	Primary 0.05	<u>QC</u> 0.10
	4/14	ND (ND)	ND	ND (ND)	ND	ND (ND)	ND	ND (ND)	ND	ND (ND)	ND
	5/16	9.3	NS	ND	NS	0.70	NS	0.079	NS	1.033	NS
	5/18	[8.2]	11.9	0.6	1.20	0.42	0.368	ND	ND	0.245	0.28
	5/23	[15.4]	NS	[0.8]	NS	0.67	NS	0.0560	NS	ND	NS
	5/25	25	32.9	0.7	0.870	ND	0.329	0.0675	ND	ND	ND
	5/30	19	NS	1.2	NS	ND	NS	ND	NS	ND	NS
	6/1	18	16.5	2.3	2.68	0.56	0.355	ND	ND	ND	ND
	6/6	16.5 (11.8)	NS	1.3 (1.2)	NS	0.45 (0.44)	NS	ND (ND)	NS	ND (ND)	NS
	6/8	17.8 (17.4)	18.4	3.5 (3.8)	3.7	0.34 (ND)	0.260	ND (ND)	ND	ND (ND)	ND
22	6/13	10.7 (10.7)	NS	1.7 (1.8)	NS	0.39 (0.35)	NS	ND (ND)	NS	ND (ND)	NS
	6/15	13.9	13.3	8.0	0.872	ND	ND	ND	ND	ND	ND
	6/20	10.4	NS	0.5	NS	ND	NS	ND	NS	ND	NS
	6/22	8.5	10.1	0.5	0.758	0.40	ND	ND	ND	ND	ND
	6/27	8.0	NS	1.8	NS	ND	NS	ND	NS	ND	NS
	6/29	10	14.2	1.4	2.17	ND	0.314	ND	ND	ND	ND
	7/3	8.5	NS	0.5	NS	ND	NS	ND	NS	ND	NS
•	7/6	5.1	5.23	0.6	0.682	ND	0.141	ND	ND	ND	ND
	7/11	9.8	NS	ND	NS	ND	NS	ND	NS	ND	NS
	7/13	3.2	3.19	ND	0.5	ND	0.124	ND	ND	ND	ND
	7/18	3.3	NS	ND	NS	ND	NS	ND	NS	ND	NS
	7/20	2.8	2.9	ND	ND	ND	0.178	ND	ND	ND	ND

Results in parentheses from samples collected by Klienfelder, Inc. Results in brackets are the results of backup sample analyses

QC Quality Control
Blank Cells Results not yet reported

ND Not Detected NS Not Sampled

#### Performance goals (ppb):

molinate	10	methyl parathion	0.13	PRELIMINARY DATA
thiobencarb	1.5	malathion	0.1	SUBJECT TO CHANGE
carbofuran	0.4			

**Table 4. 1995 Pesticide Concentrations at Butte Slough at Lower Pass Road in Sutter County in parts per billion (ppb)**Samples collected by Klienfelder, Inc.

	Molinate	Thiobencarb	Carbofuran	Methyl parathion	Malathion
<u>Date</u>	Primary	Primary	Primary	Primary	Primary
4/14	ND	ND	ND	ND	ND
5/16	ND	ND	ND	ND	ND
5/2 <b>3</b>	[ND]	ND	ND	ND	ND
5/30	6.4	ND	0.57	ND	ND
6/1	· 7.4	ND	ND	0.187	ND
6/6	8.4	ND	0.37	ND	ND
6/8	6.1	ND	ND	ND	ND
6/13	3.4	ND	ND	ND	ND
6/15	3.9	1.1	ND	ND	ND
6/20	8.5	ND .	0.37	ND	ND
6/22	6.3	1.3	ND	ND	ND
6/27	7.3	ND	ND	ND	0.639
6/29	7.0	ND	ND	ND	ND
7/3	6.2	ND	0.5	ND	ND
7/6	3.1	ND	ND	ND	ND
7/11	2.7	ND	ND	ND	ND
7/18	2.1	ND	ND	ND	ND

Results in brackets are the results of backup sample analyses.

Blank Cells Results not yet reported

ND Not Detected

Performance goals (ppb):

molinate 10
thiobencarb 1.5
carbofuran 0.4
methyl parathion 0.13
malathion 0.1

PRELIMINARY DATA--SUBJECT TO CHANGE

**Table 5. 1995 Pesticide Concentrations at the Sacramento River at the Village Marina in Sacramento County in parts per billion (ppb)**Samples collected by Klienfelder, Inc.

	Molinate	Thiobencarb	Carbofuran	Methyl parathion	Malathion
<u>Date</u>	<b>Primary</b>	Primary	Primary	Primary	Primary
4/14	ND	ND	ND	ND	ND
5/16	ND	ND	ND	ND	ND
5/23	[ND]	ND	ND	ND	ND
5/30	ND	ND	ND	ND	ND
6/1	ND	ND	ND	ND	ND
6/6	ND	ND	ND	ND	ND
6/8	ND	ND	ND	ND	ND
6/13	ND	ND	ND	ND	ND
6/15	ND	ND	ND	ND	ND
6/20	ND	ND	. ND	ND	ND
6/22	ND	ND	ND	ND	ND
6/27	ND	ND	ND	ND	ND
6/29	ND	ND	ND	ND	ND
7/3	ND	ND	ND	ND	ND
7/6	ND	ND	ND	ND	ND
7/11	ND	ND	ND	ND	ND
7/18	ND	ND	ND	ND	ND

Results in brackets are the results of backup sample analyses. Blank Cells Results not yet reported ND Not Detected

#### Performance goals (ppb):

molinate	10
thiobencarb	1.5
carbofuran	0.4
methyl parathion	0.13
malathion	0.1

PRELIMINARY DATA--**SUBJECT TO CHANGE** 

**Table 6.** Concentrations of molinate and thiobencarb in the Sacramento River at the intake to the City of Sacramento water treatment facility (SRRAW) in 1995.

	Concentr	Concentration (ppb)			
<u>Date</u>	<u>molinate</u>	thiobenearb			
5/17	$ND^2$	ND			
5/22	ND	ND			
5/25	ND	ND			
5/29	0.12	ND			
6/01	ND	ND			
6/05	ND	ND			
6/09	ND	ND			
6/12	ND	ND			
6/15	ND	ND			
6/19	ND	ND			
6/22	0.16	ND			
6/26	ND	ND			
6/30	ND	ND			

- 1. Samples collected and analyzed by the City of Sacramento.
- 2. ND None detected. Limit of detection = 0.10 ppb.

**Table 7.** Peak molinate concentrations in selected Sacramento Valley waterways<sup>1</sup> in 1981 - 1995.

		<u>(</u>	Concentra	ition (ppb)	
Year	CBD1	CBD5	<u>SS1</u>	<u>BS1</u>	SR1
1981	340	357	2		
1982	204	697		187	27
1983	211	228	68		7
1984	110	120	44		21
1985	95	100	49		16
1986	77	88	30		11
1987	43	53	22	44	7.6
1988	67	89	30	52	8.0
1989	51	60	30	43	6.0
1990	51	59	40	36	8.9
1991	18	17	9.6	26	1.3
1992	6.2	24	15	26	$ND^3$
1993	$69.1^{4}$	96.1	31.2	39.2	2.59
1994	21	57	9.8	18.3	
1995		25		8.5	$ND^3$

Colusa Basin Drain at Roads 109 and 99E near Knight's Landing in Yolo
County.
Colusa Basin Drain at or near Highway 20 in Colusa County.
Sacramento Slough at DWR gauge station in Sutter County.
Butte Slough at Highway 20 in Sutter County.
Sacramento River at Village Marina in Sacramento County.

- 2. Blanks indicate no data are available.
- 3. ND None detected. Method detection limit = 1.0 ppb.
- 4. Mean of duplicate analyses.

**Table 8.** Peak thiobenearb concentrations in selected Sacramento Valley waterways<sup>1</sup> in 1981 - 1994.

			Concent	ration (ppl	2)
<u>Year</u>	CBD1	CBD5	<u>SS1</u>	<u>BS1</u>	SR1
1981	21	23	2		
1982	57	170		10	6
1983	11.3	9.0	4.9		0.8
1984	7.5	14.0	7.8		1.0
1985	19	18	П		4.1
1986	7.4	6.9	3.8		1.1
1987	3.7	1.5	0.6	$ND_3$	ND
1988	4.5	0.6	ND	1.0	ND
1989	1.34	0.55	ND	0.98	ND
1990	ND	ND	ND	2.0	ND
1991	ND	ND	ND	ND	ND
1992	5.7	6.7	2.0	9.7	ND
1993	4.87	3.68	ND	ND	ND
1994	15.8	$37.4^{4}$	ND	0.53	
1995		3.5		1.3	ND

1.CBD1	Colusa Basin Drain at Roads 109 and 99E near Knight's Landing in
	Yolo County.
CBD5	Colusa Basin Drain at Highway 20 in Colusa County.
SS1	Sacramento Slough at DWR gauge station in Sutter County.
BS1	Butte Slough at Highway 20 in Sutter County.
SR1	Sacramento River at Village Marina in Sacramento County.

- 2. Blanks indicate no data are available.
- 3. ND Not detected. Different detection limits (lowest quantifiable concentrations) were reported during this period, all of which were less than or equal to 1.0 ppb.
- 4. A second extraction and analysis was conducted with a result of 40.3 ppb.

## Appendix A

State of Califori

Pete Wilson, to.

## DEPARTMENT OF PESTICIDE REGULATION James W. Wells, Director

1020 M Street, Room 100 Cacramento, California 36814-5604

March 8, 1995

TO:

COUNTY AGRICULTURAL COMMISSIONERS

IN RICE-GROWING COUNTIES OF THE SACRAMENTO VALLEY

SUBJECT: 1995 RICE PESTICIDES PROGRAM

On January 27, 1995, the Central Valley Regional Water Quality Control Board (CVRWQCB) approved management practices that limit discharges of the rice pesticides molinate (Ordram³), thiobencarb (Bolero³ and Abolish³), carbofuran (Furadan³), methyl parathion, and malathion to surface waters. The CVRWQCB staff sent you a copy of the agenda item for this meeting along with a report prepared by my staff entitled: "Information on Rice Pesticides Submitted to the Central Valley Regional Water Quality Control Board" (December 28, 1995). This letter contains details on the 1995 rice pesticide program including conditions you are asked to implement for rice pesticide permits.

Most of the provisions of the rice pesticide program relating to routine water-holding times will remain the same as in 1994. However, changes will apply for regions previously considered hydrologically isolated to ensure compliance with the CVRWQCB's prohibition of acutely toxic discharges to waters that support aquatic habitat.

In addition, the CVRWQCB approved management plans to promote an educational effort with the rice-growing community that stresses the continued importance of drift prevention and introduces the potential contributions seepage water makes to the pesticide concentrations in the agricultural drains. Drift control provisions remain as they were in 1994. Continue to have your staff impress upon commercial applicators the need to better control applications of pesticides near agricultural drains and focus additional enforcement efforts, when possible, on aerial applications made to fields adjacent to agricultural drains. My



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staff is working with representatives from the rice-growing community to propose voluntary measures growers might take to prevent rice field seepage water from entering surface waterways prior to the end of the required holding periods for field water. Your assistance in distributing forthcoming information to growers on seepage water containment will be appreciated.

The key features of the 1995 program are as follows:

- 1. The basic water management requirements for users of those pesticides that require permits (molinate, thiobencarb, methyl parathion, and carbofuran) are the same as in 1994. The water management requirements for the 1995 program as approved by the CVRWQCB are outlined in Attachments 1-4. Holding times for all applications (not just the "preflood surface" applications) of Abolish decreased to 19 days. Areas considered hydrologically isolated must hold water from fields treated with molinate and thiobencarb for longer periods (11 and 19 days, respectively) than previously required. Exceptions for some fields treated with thiobencarb are described in Attachment 2.
- 2. The water management practices following malathion use in rice are still voluntary. Attachment 5, which describes these practices, was designed to be distributed to growers.
- 3. Management practices for containing seepage water from rice fields and the pesticides this water may contain will be addressed through forthcoming educational measures and implemented through voluntary efforts by growers.
- 4. Water management practices within closed systems remain the same for 1995. The Department of Pesticide Regulation (DPR) will conduct a study on toxicity of water in multigrower closed systems to determine any need for longer holds in future years.

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March 9, 1999
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- The emergency release provisions remain the same as in 1994 to continue to meet the CVRWQCB's prohibition of acutely toxic discharges to waters that support aquatic habitat. Growers with fields treated with Ordram may apply for an emergency release after a minimum holding period of 11 days. Fields will be prohibited from using the emergency release management option until the standard holding times for the insecticides have elapsed. Fields treated with Bolero do not qualify for the emergency release option. Attachment 6 is the form which permittees are to fill out as part of their request for an emergency release. Those that are granted an emergency release must also fill out an additional form (Attachment 7) and deliver it to your office. Failure to submit this form will be considered a permit violation. DPR staff will request the information on the completed forms later this summer.
- 6. Growers using the emergency release provision more than once or cited for water holding violations more than once must make improvements in water management capabilities. Such improvements will be required as conditions on future pesticide use permits and may include retention basins, ponds, or tailwater recovery systems.
- 7. Drift control provisions will again be an important part of the program. Methyl parathion application provisions are the same as in 1994. They include the use of an effective drift control agent, use of D8 nozzles, wind speeds ≤ 5 miles per hour, and a 300-foot downwind buffer zone left untreated. Attachments 8, 9, 10, and 11 outline the provisions for aerial applications of granular and liquid formulations of rice pesticides included in the program. Special attention should be directed, when possible, towards enforcement efforts during aerial applications at sites adjacent to agricultural drains.
- 8. Weir boxes that control discharges of water from rice fields shall be fully secured during pesticide holding times. A soil berm must be in place in front of each of these boxes

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to a level above the water line, or drop boxes shall be filled with soil to a level above the water line. The need for such berms in fields where nonconventional water management systems are utilized, e.g., static/positive pressure systems, may be evaluated by County Agricultural Commissioner's office staff on a case-by-case basis.

Information transmittal of rice pesticide use data from the county offices to DPR will be handled at the end of July rather than on a weekly basis. My staff will discuss the details of this process with your deputies.

Monitoring results will not be available this year until approximately five weeks after sample collection. DPR will continue to send monitoring program results to your offices, via facsimile, when available.

Thank you for your assistance. Your cooperation continues to help make the program a real success. If you have questions, please contact Dr. Nan Gorder at (916) 324-4265 or Mr. Marshall Lee at (916) 324-4269.

Sincerely,

James W. Wells

Director

(916) 445-4000

cc: Dr. Nan Gorder

Mr. Marshall Lee

### MOLINATE WATER MANAGEMENT REQUIREMENTS - 1995

- All water from fields treated with products containing molinate must be retained on the site of application for at least 28 days following application unless:
  - A. The water is contained within a tailwater recovery system, ponded on fallow land, or contained in other systems appropriate for preventing discharge. The system may discharge 29 days following the last application of molinate within the system.
    - 1. If the system is under the control of one permittee, water may be discharged from the application site in a manner consistent with product labeling.
    - 2. If the system includes drainage from more than one permittee, water may be discharged from the application site into the system nine days following application.
  - B. The water is on acreage within the bounds of areas that discharge negligible amounts of rice field drainage into perennial streams until fields are drained for harvest. All water on fields treated with molinate must be retained on the treated acreage until the twelfth day following application.
  - C. The water is on acreage treated with a preflood application of molinate. The label restrictions apply.
- II. Fields not specified in I.A., I.B., and I.C. may resume discharging field water 29 days following application at a volume not to exceed two inches of water over a drain box weir. Unregulated discharges from these fields may then resume after seven days.

### MOLINATE WATER MANAGEMENT REQUIREMENTS - 1995

III. The county agricultural commissioner may authorize the emergency release of tailwater 12 days following the last molinate application, following a review of a written request (Attachment 6) which clearly demonstrates the crop is suffering because of the water management requirements. All water management requirements must be followed that are associated with other pesticides that may have been applied to the site. Additionally, the requester must describe preventative action that would avoid the need for future emergency releases. Under an emergency release variance, tailwater may be released only to the extent necessary to mitigate the documented problem. Those issued an emergency release must submit to the county agricultural commissioner a report (Attachment 7) indicating the time and duration of the emergency release and data that can be used to calculate the total amount of water released during the emergency release. Emergency release will only be granted for reasons related to rainfall, high winds, or other extreme weather conditions that cannot be moderated with management practices.

# THIOBENCARB WATER MANAGEMENT REQUIREMENTS - 1995 Revised April 7, 1995

- I. For rice fields treated with thiobencarb in the Sacramento Valley (north of the line defined by Roads E10 and 116 in Yolo County and the American River in Sacramento County), except those treated with Abolish 8EC:
  - A. All water on treated fields must be retained on the treated fields for at least 30 days following application unless:
    - 1. The water is contained within a tailwater recovery system, ponded on fallow land, or contained in other systems appropriate for preventing discharge. The system may discharge 20 days following the last application of thiobencarb within the system.
      - a. If the system is under the control of one permittee, water may be discharged from the application site in a manner consistent with product labeling.
      - b. If the system includes drainage from more than one permittee, water may be discharged from the application site into the system seven days following application.
    - 2. The water is on fields within the bounds of areas that discharge negligible amounts of rice field drainage into perennial streams until fields are drained for harvest. Water from such fields must be held at least 19 days, unless the county agricultural commissioner evaluates such sites. If the commissioner verifies the hydrologic isolation of the fields, the water may be released seven days after application.

# THIOBENCARB WATER MANAGEMENT REQUIREMENTS - 1995 Revised April 7, 1995

- B. Fields not specified in I.A.1. and I.A.2. may resume discharging field water 31 days following application at a volume not to exceed two inches of water over a drain box weir. Unregulated discharges from these fields may then resume after seven days.
- II. For rice fields treated with thiobencarb in the Southern Area (south of the line defined by Roads E10 and 116 in Yolo County and the American River in Sacramento County), except those treated with Abolish 8EC:
  - A. All water on treated fields must be retained on the treated fields for at least 19 days following application unless:
    - 1. The water is contained within a tailwater recovery system, ponded on fallow land, or contained in other systems appropriate for preventing discharge. The system may discharge 20 days following the last application of thiobencarb within the system.
      - a. If the system is under the control of one permittee, water may be discharged from the application site in a manner consistent with product labeling.
      - b. If the system includes drainage from more than one permittee, water may be discharged from the application site into the system seven days following application.

# THIOBENCARB WATER MANAGEMENT REQUIREMENTS - 1995 Revised April 7, 1995

- 2. The water is on fields within the bounds of areas that discharge negligible amounts of rice field drainage into perennial streams until fields are drained for harvest. Water from such fields may be released seven days after application if the county agricultural commissioner evaluates such sites and verifies the hydrologic isolation of the fields.
- B. Fields not specified in II.A.1. and II.A.2. may resume discharging field water 20 days following application at a volume not to exceed two inches of water over a drain box weir. Unregulated discharges from these fields may then resume after seven days.

### III. For all areas, fields treated with Abolish 8EC:

- A. All water on treated fields must be retained on the treated fields for at least 19 days following application unless:
  - 1. The water is contained within a tailwater recovery system, ponded on fallow land, or contained in other systems appropriate for preventing discharge. The system may discharge 20 days following the last application within the system.
    - a. If the system is under the control of one permittee, water may be discharged from the application site in a manner consistent with product labeling.
    - b. If the system includes drainage from more than one permittee, water may be discharged from the application site into the system seven days following application.

# THIOBENCARE WATER MANAGEMENT REQUIREMENTS - 1995 Revised April 7, 1995

- 2. The water is on fields within the bounds of areas that discharge negligible amounts of rice field drainage into perennial streams until fields are drained for harvest. Water from such fields may be released seven days after application if the county agricultural commissioner evaluates such sites and verifies the hydrologic isolation of the fields.
- B. Fields not specified in III.A. may resume discharging field water 20 days following application at a volume not to exceed two inches of water over a drain box weir. Unregulated discharges from these fields may then resume after seven days.

### CARBOFURAN WATER MANAGEMENT REQUIREMENTS - 1995

- I. Pre-flood applications of carbofuran to rice fields must be incorporated into the soil.
- II. Water shall not be discharged from sites treated with carbofuran for at least 28 days following initial flooding (pre-flood application) or following application (post-plant application) unless the treated water is contained within tailwater recovery systems, ponded on fallow land, or contained in other systems appropriate for preventing discharge. The system may discharge 29 days following the last application of carbofuran within the system.
  - A. If the system was under the control of one permittee, treated water may be discharged from the application site in a manner consistent with product labeling.
  - B. If the system includes drainage from more than one permittee, treated water may be discharged from the application site into the system nine days following application.

### METHYL PARATHION WATER MANAGEMENT REQUIREMENTS - 1995

Water shall not be discharged from sites treated with methyl parathion for at least 24 days following application unless the treated water is contained within a tailwater recovery system, ponded on fallow land, or contained in other systems appropriate for preventing discharge. The system may discharge 25 days following the last application of methyl parathion within the system. Treated water may be discharged from the application site in a manner consistent with product labeling.

### MALATHION WATER MANAGEMENT REQUIREMENTS - 1995

The Central Valley Regional Water Quality Control Board has approved a water management practice following malathion use in rice that will help meet 1995 water quality performance goals for malathion in surface water. Malathion is currently not a restricted material and not subject to use requirements or permit conditions. However, it is important that growers comply with this practice.

Water from fields treated with malathion should be held on the site of application for at least four days following application.

Water quality monitoring will be conducted in 1995 to determine the adequacy of this practice in managing malathion discharges. If malathion levels do not adequately meet the performance goal, a more formal regulatory program may be implemented in future years.

### **EMERGENCY RELEASE**

Grower:		Permit No.:			
Address:					
Field location:		Site No.:			
(Attach detailed map)					
Chemical applied:		Chemical a	pplied:		
Rate of application:		Rate of app	lication:		
Date of application:		Date of app	lication:		
Average water depth		Average wa	iter depth:		
at time of application:		at time of a	pplication:		
Chemical applied:		Chemical a	pplied:		
Rate of application:					
Date of application:					
Average water depth		Average wa	ter depth	_	
at time of application:		Average water depthat time of application:			
Starting date of emergency	release:			·	
Acres in field:		Laser leveled?	Yes	No	
Type of irrigation system:	Flow through_	Recycle	Static	Other	
Date flooding began:	N	o. of days it takes to	fill field:		
Describe problem that led to	_	ase:			
Steps that can be taken to pr	event emergency			/ears:	
Recommendation (attached)	by:				
Applications by:					
Grower's signature:			Date:		
Approved by:		Agricultural Dista	a iat		
		Agricultural Biolo	gist		

### EMERGENCY RELEASE

Grower.	<del></del>			Permit No.: _		
Address:				Zip:		
Field location:				Site No.:		
Beginning date of release:				Ending date:		
To do this, mea	isure the width o	of each weir ope	ned to allow the	ring the emergen discharge. Then I information in t	cy release period, , on a daily basis, the table below.	
W	eir l	/eir 2	Weir 3			
   Width:		   Width:		   Width:		
Date	Height of water	Date	Height of water	Date	Height of water	
<u> </u>				<u> </u>		
			<u> </u>			
	 		<u> </u>	<u> </u>	]	
	<u> </u>	<u> </u>	<u> </u>	<u> </u>		
			<u> </u>	<u> </u>	<u> </u>	
			<u> </u>	-		
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DRIFT CONTROL REQUIREMENTS FOR GRANULAR MOLINATE, THIOBENCARB, AND CARBOFURAN APPLIED TO RICE - 1995

Granular molinate, thiobencarb, or carbofuran drifting into waterways (i.e., drainage canals) or onto levees or roadways adjacent to waterways will be considered environmental contamination. Applicators found in violation will be liable for a civil penalty.

Granular molinate, thiobencarb, or carbofuran shall not be applied by air if wind speed is greater than seven miles per hour to avoid drift into drainage canals and ditches.

# DRIFT CONTROL REQUIREMENTS FOR LIQUID THIOBENCARB APPLIED TO RICE - 1995

#### I. Aerial Applications

- A. No aerial applications of liquid formulations of thiobencarb to rice shall be:
  - 1. Discharged more than ten feet above the crop or target. Discharge shall be shut off whenever it is necessary to raise the equipment over obstacles such as trees or poles.
  - 2. Applied when wind velocity is more than seven miles per hour.
  - 3. Applied by aircraft except as follows:
    - a. The flow of liquid to aircraft nozzles shall be controlled by a positive shutoff system as follows:
      - i. Each individual nozzle shall be equipped with a check valve and the flow controlled by suckback device or a boom pressure release device; or
      - ii. Each individual nozzle shall be equipped with a positive action valve.
    - b. Aircraft nozzles shall not be equipped with any device or mechanism which would cause a sheet, cone, fan, or similar type dispersion of the discharged material except as otherwise provided.
    - c. Aircraft boom pressure shall not exceed 40 pounds per square inch.
    - d. Aircraft nozzles shall be equipped with orifices directed backward parallel to the horizontal axis of the aircraft in flight.

## DRIFT CONTROL REQUIREMENTS FOR LIQUID THIOBENCARB APPLIED TO RICE - 1995

- e. Fixed wing aircraft and helicopters operating in excess of 60 miles per hour shall be equipped with jet nozzles having an orifice of not less than 1/16 inch diameter.
- f. Working boom length on fixed wing aircraft shall not exceed 3/4 of the wing span; the working boom length of helicopters shall not exceed 6/7 of the total rotor length or 3/4 of the total rotor where the rotor length exceeds 40 feet.
- g. Helicopters operating at 60 miles per hour or less shall be equipped with:
  - i. Nozzles having an orifice not less than 1/16 inch in diameter. A number 46 (or equivalent) or larger whirlplate may be used; or
  - ii. Fan nozzles with a fan angle number not larger than 80 degrees and a flow rate not less than one gallon per minute at 40 pounds per square inch pressure (or equivalent).
- B. Special precautions should be taken to avoid off-site deposition of liquid formulations of pesticides when applications are made adjacent to agricultural drains.
- II. Ground Applications Ground applications of liquid thiobencarb must be applied as per label instructions.

## DRIFT CONTROL RECOMMENDATIONS FOR MALATHION APPLIED TO RICE - 1995

- I. No aerial applications of liquid formulations of malathion to rice shall be:
  - A. Discharged more than ten feet above the crop or target. Discharge shall be shut off whenever it is necessary to raise the equipment over obstacles such as trees or poles.
  - B. Applied when wind velocity is more than seven miles per hour.
  - C. Applied by aircraft except as follows:
    - 1. The flow of liquid to aircraft nozzles shall be controlled by a positive shutoff system as follows:
      - a. Each individual nozzle shall be equipped with a check valve and the flow controlled by suckback device or a boom pressure release device; or
      - b. Each individual nozzle shall be equipped with a positive action valve.
    - 2. Aircraft nozzles shall not be equipped with any device or mechanism which would cause a sheet, cone, fan, or similar type dispersion of the discharged material except as otherwise provided.
    - 3. Aircraft boom pressure shall not exceed 40 pounds per square inch.
    - 4. Aircraft nozzles shall be equipped with orifices directed backward parallel to the horizontal axis of the aircraft in flight.

## DRIFT CONTROL RECOMMENDATIONS FOR MALATHION APPLIED TO RICE - 1995

- 5. Fixed wing aircraft and helicopters operating in excess of 60 miles per hour shall be equipped with jet nozzles having an orifice of not less than 1/16 inch diameter.
- 6. Working boom length on fixed wing aircraft shall not exceed 3/4 of the wing span; the working boom length of helicopters shall not exceed 6/7 of the total rotor length or 3/4 or the total rotor where the rotor length exceeds 40 feet.
- 7. Helicopters operating at 60 miles per hour or less shall be equipped with:
  - a. Nozzles having an orifice not less than 1/16 inch in diameter. A number 46 (or equivalent) or larger whirlplate may be used; or
  - b. Fan nozzles with a fan angle number not larger than 80 degrees and a flow rate not less than one gallon per minute at 40 pounds per square inch pressure (or equivalent).
- II. Special precautions should be taken to avoid off-site deposition of liquid formulations of pesticides when applications are made adjacent to agricultural drains.

# DRIFT CONTROL REQUIREMENTS FOR METHYL PARATHION APPLIED TO RICE - 1995

#### I. Aerial Applications

- A. No aerial applications of liquid formulations of methyl parathion to rice shall be:
  - 1. Discharged more than ten feet above the crop or target. Discharge shall be shut off whenever it is necessary to raise the equipment over obstacles such as trees or poles.
  - 2. Applied within a 300 foot downwind buffer zone from any agricultural drain.
  - 3. Applied when wind velocity is more than five miles per hour.
  - 4. Applied without an effective drift control agent.
  - 5. Applied by aircraft except as follows:
    - a. The flow of liquid to aircraft nozzles shall be controlled by a positive shutoff system as follows:
      - i. Each individual nozzle shall be equipped with a check valve and the flow controlled by suckback device or a boom pressure release device; or
      - ii. Each individual nozzle shall be equipped with a positive action valve.
    - b. Aircraft nozzles shall not be equipped with any device or mechanism which would cause a sheet, cone, fan, or similar type dispersion of the discharged material except as otherwise provided.

## DRIFT CONTROL REQUIREMENTS FOR METHYL PARATHION APPLIED TO RICE-1995

- c. Aircraft boom pressure shall not exceed 40 pounds per square inch.
- d. Aircraft nozzles shall be equipped with orifices directed backward parallel to the horizontal axis of the aircraft in flight.
- e. Fixed wing aircraft and helicopters operating in excess of 60 miles per hour shall be equipped with jet nozzles having an orifice of not less than 1/8 inch diameter.
- f. Working boom length on fixed wing aircraft shall not exceed 3/4 of the wing span; the working boom length of helicopters shall not exceed 6/7 of the total rotor length or 3/4 of the total rotor where the rotor length exceeds 40 feet.
- g. Helicopters operating at 60 miles per hour or less shall be equipped with:
- i. Nozzles having an orifice not less than 1/8 inch in diameter. A number 46 (or equivalent) or larger whirlplate may be used;
- ii. Fan nozzles with a fan angle number not larger than 80 degrees and a flow rate not less than one gallon per minute at 40 pounds per square inch pressure (or equivalent).
- B. Special precautions should be taken to avoid off-site deposition of liquid formulations of pesticides when applications are made adjacent to agricultural drains.

# DRIFT CONTROL REQUIREMENTS FOR METHYL PARATHION APPLIED TO RICE-1995

- II. Ground Applications Ground equipment other than handguns shall be equipped with
  - A. Nozzles having an orifice not less than 1/16 inch in diameter or equivalent, and operated at a boom pressure not to exceed 30 pounds per square inch; or
  - B. Low pressure fan nozzles with a fan angle number not larger than 80 degrees and fan nozzle orifice not smaller than 0.2 gallon per minute flow rate or equivalent, and operated at a boom pressure not to exceed 15 pounds per square inch.

# Appendix B

APPENDIX B

RICE PESTICIDES PROGRAM: REQUIRED HOLDING TIMES (1994 and 1996) (1994 represents the most recent program different from the 1995 and 1996 program.)

		HOI	DING TIME	S (days)			
		5	SACRAMENTO VALLEY			SAN JOAQUIN VALLEY	
		Standard Hold	Water- short Areas*	Hydrolog- ically Isolated Fields	Standard Hold	Hydrolog- ically Isolated Fields	
Molinate	1994	28	8	-	8	-	
	1996	28	11	11	11	11	
Thiobencarb:							
Bolero	1994	30	6	-	6	-	
	1996	30	19	6	19	6	
Abolish	1994	19, preflood 30, pinpoint & drill seeded	6	-	6	-	
	1996	19, all applications	19	6	19	6	
Carbofuran	1994	28	•	•	28	-	
·	1996	28	-	-	28	-	
Methyl parathion	1994	24	•	-	24	•	
	1996	24	•	-	24	-	
Malathion	1994	4, voluntary	•	-	4, voluntary	-	
	1996	4, voluntary	•	-	4, voluntary	•	

<sup>\*</sup>Water-short areas of the Sacramento Valley include Placer County and parts of western Yolo County.

Closed systems (tailwater recovery systems) and water ponded on fallow land must meet different (shorter) holding times than indicated on this table. The program requirements for these areas are the same for the 1994 and 1996 programs.

# Appendix C

#### Memorandum

To : County Agricultural Commissioners from

Date: March 24, 1995

Rice Producing Counties

Place: Sacramento

Phone: (916) 324-4265

m : Department of Pesticide Regulation · John Sanders, Branch Chief

Environmental Monitoring and Pest Management

Subject : Rice Pesticides Program

Follow-up on Seepage Water Management Voluntary Guidelines

The 1995 rice pesticide permit conditions were recently mailed to you office with a cover letter dated March 20 and signed by Jim Wells. That letter referred to forthcoming information regarding voluntary guidelines for seepage water management. My staff, with input from representatives of the rice industry, county agricultural commissioners, United States Department of Agriculture (USDA), and others, developed the attached seepage water management voluntary guidelines which are meant to be reproduced and handed out when issuing permits for the use of rice pesticides. Your assistance in this matter is greatly appreciated.

Additionally, for growers interested in technical specifications on berm construction, a second handout is provided from the USDA Natural Resources Conservation Service entitled "Closed Rice Water Management Systems". This handout was developed for the California Rice Water Quality Demonstration Project to describe specifications for various closed systems, but it includes useful technical specifications for sound berm construction as well. We are supplying you with cameraready copies of this handout so your office can make good reproductions for interested growers.

Should you have any questions, please contact Nan Gorder at (916) 324-4265 or Marshall Lee at (916) 324-4269.

John S. Sander

Branch Chief

(916) 324-4100

#### SEEPAGE WATER MANAGEMENT: VOLUNTARY GUIDELINES

#### What is seepage?

Movement of water through a rice field levee to an adjacent area.

#### Why is seepage water a problem?

Seepage water can contain high concentrations of molinate, carbofuran, and potentially other chemicals as well, during the holding periods. If this water is allowed to reach agricultural drains, it could impact efforts to meet performance goals and result in toxicity to aquatic organisms.

#### What evidence is there to indicate seepage water contains pesticides?

Molinate was detected in rice seepage water from six out of six sites with concentrations ranging from 44 to 1300 parts per billion (ppb). Carbofuran was detected in rice seepage water collected from three out of three sites with concentrations ranging from 0.4 to 11 ppb. (Water samples were simultaneously collected from adjacent fields and carbofuran concentrations were as high or higher than in seepage water.) The current performance goal in the agricultural drains for molinate is 10 ppb and for carbofuran is 0.4 ppb.

Two demonstration sites were set up with tarps covering the seepage area to prevent molinate deposition from drift. Concentrations of molinate from these sites ranged from 37 to over 700 ppb (corrected for background concentrations).

### Why are growers being asked to make voluntary efforts to control seepage water?

The Central Valley Regional Water Quality Control Board and the Department of Pesticide Regulation believe it is important that the rice growing community become aware of the potential impact of contaminated seepage water reaching the agricultural drains and have the opportunity to voluntarily address the problem. If these voluntary efforts are sufficient to minimize the impact of seepage water on the agricultural drains, no future regulatory action will be needed.

#### **VOLUNTARY GUIDELINES**

- 1. Prevent seepage water from leaving the rice field during the holding period through loosely constructed levees by
  - running a tractor tire or track on top of existing border levees, and
  - ensuring that newly constructed levees are built with mineral soils (not organic matter and plant residues), adequate width, and solid cores (when building levees, run tractor tire or track on top to firm up core of check). Double berming is another method of containing seepage.
  - using technical recommendations for levee construction offered by the USDA in a handout entitled
     "Closed Rice Water Management Systems," available from your county agricultural commissioner.
- 2. Prevent water in seepage areas from reaching the drains during the holding period by
  - directing or pumping seepage water to fallow land, and
  - blocking the exit of water from the seepage ditch to agricultural drains.
- 3. Communicate with applicators to establish the common goal of keeping drift away from seepage ditches, drains, border levees, and roads. Dry material on roads and dry ground is considered to be environmental contamination with the applicator liable for a civil penalty. This material remains viable and any runoff from these areas during wet weather should be held on your property to avoid contaminating agricultural drains.
- 4. Prevent leakage from levees by inspecting and repairing rodent damage during the holding periods.

tion and adjustments in basin water depth. A pump with pipeline or return ditch is used to convey the tail water back to an upper level rice basin. The minimum sump storage requirement shall be the volume of runoff generated by the normal flow off the bottom weir for 12 hours or 20 percent of the irrigation inflow for 12 hours, whichever is greater. The recirculating pump shall have a capacity equal to or greater than the mean inflow rate.

Static Water Systems - Systems that independently supply water to each basin within the field. Flap-gated inlet pipes or other devices keep pesticide treated water on the field and out of public water ways. It operates on the principle of a variable demand supply, only the amount of water needed to replace evapotranspiration and other losses is placed in each basin either from:

- (i) a source ditch with flashboard weirs in the ditch and flap-gated inlet pipes into each basin, or
- (ii) a pipeline or ditch with adjustable inlet float control valves into each basin.

Irrigation water in the supply ditch shall be protected from contamination by means of flap gates and other such anti-back flow devices as are appropriate. The flap gates help to keep pesticide treated field water out of the supply ditch and out of public waterways. The capacity of the static system shall be adequate to flood up the basin to the desired depth in 3 days or less.

#### SYSTEM OPERATION -

The owner or producer is responsible for the preparation and implementation of an operation and maintenance plan. The plan will include sufficient instructions to insure that the system achieves its intended purpose.

Revised 11/94

#### USDA NRCS Design Standards:

587 - Water Control Structures

430 - Irrigation Pipelines

388 - Field Ditches

356 - Dikes

464 - Land Leveling

206 - Rice Water Management Systems

#### Contact your local USDA Natural Resources Conservation Service:

Auburn	(916) 823-6830
Colusa	(916) 458-2931
Willows	(916) 934-4601
Woodland	(916) 662-2037
Yuba City	(916) 674-1461

Contact your local USDA Consolidated Farm Services Agency for cost-sharing information.

Contact your local U.C. Cooperative Extension Office or ANR Publications at (510) 642-2431 for the following publications:

Rice Irrigation Systems for Irrigation Water Management. Cooperative Extension, University of California, 1994 Pub #21490

Rice Production in California. Cooperative Extension, University of California, 1992 Pub #21498

Integrated Pest Management for Rice. Second Edition, University of California, Statewide IPM project. 1993 Pub # 3280

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To file a complaint, write the Secretary of Agriculture, U.S. Department of Agriculture, Washington, D.C. 20250, or call (202) 720-7327 (voice) or (202) 720-1127 (TDD). USDA is an equal opportunity employer.



Engineering Standards and Specifications for

# Closed Rice Water Management Systems

# California Rice Water Quality Demonstration Project

U.S. Natural Resources
Conservation Service

in cooperation with University of California, Cooperative Extension and the Consolidated Farm Services Agency

# Appendix D

California Environmental Protection Agency
Department of Pesticide Regulation
Environmental Monitoring and Pest Management
1020 N Street, Room 161
Sacramento, California 95814
December 14, 1994
Revised March 1, 1995

#### 1995 RICE PESTICIDES MONITORING PROTOCOL

#### I. Introduction

In the late 1970's and early 1980's, fisheries biologists from the California Department of Fish and Game (CDFG) observed extensive fish kills, involving primarily carp, in some agricultural drains in the rice growing region of the Sacramento Valley. Investigations from 1980 to 1982 by CDFG resulted in the determination that these fish kills were due to toxicity related to the rice herbicide, molinate (Ordram<sup>®</sup>) (Finlayson et al. 1982). In addition, during the summers of 1981 and 1982, the City of Sacramento also received numerous complaints about the taste of the city drinking water and later determined that the cause was another rice herbicide, thiobencarb (Bolero<sup>®</sup>) (California 1987). These pesticide related incidents were of major concern because the water in the drains is affected by agricultural practices in the Sacramento Valley, and pesticide residues in these waters contribute to the mass load of pesticides in the Sacramento River.

In an effort to mitigate these problems, CDFG, the California State Water Resources Control Board, the Central Valley Regional Water Quality Control Board, the California Department of Pesticide Regulation (DPR), formerly the California Department of Food and Agriculture (CDFA) (Division of Pest Management), county agricultural commissions and private industry are participating in a project to reduce the presence of rice pesticides in the surface waterways of the Sacramento Valley. Currently, molinate, thiobencarb, carbofuran (Furadan<sup>®</sup>), methyl parathion and malathion concentrations and water quality parameters are monitored in the agricultural drains of the Sacramento Valley each year. Surface water samples used for analyses of rice chemical concentrations were collected during the rice growing season by CDFG from 1980 to 1994 and will now be collected by DPR. CDFG will continue to perform biotoxicity testing; toxicity results will be provided by CDFG in a separate report.

During 1994 monitoring, the concentration of each of the rice pesticides – molinate, thiobencarb, carbofuran, methyl parathion and malathion – exceeded the recommended water quality performance goals for at least one of the four monitoring sites; the highest concentrations consistently occurred at the Colusa Basin Drain site number 5 (Lee 1994). Since the rice pesticide concentrations were highest at the Colusa Basin Drain site number 5 (CBD5) and because there is an established historical record of these concentrations, CBD5 will be used exclusively as a rice pesticides indicator site for the 1995 Rice Pesticides Monitoring Program. In addition to measuring pesticide

concentrations and water quality parameters, DPR will also collect water for CDFG's biotoxicity tests. The data collected in this study on pesticide residues will be used to evaluate the success of the 1995 Rice Pesticide Monitoring Program and develop any programmatic changes for the 1996 Program.

### II. Objective

The Colusa Basin Drain is important to the Rice Pesticides Monitoring Program for several reasons: (1) it receives a large volume of rice field effluent from the Sacramento Valley, (2) previous water quality data has been collected along its watercourse and (3) it is a tributary of the Sacramento River. The objective of this study is to measure the concentrations of five pesticides – molinate, thiobencarb, carbofuran, methyl parathion and malathion – in the Colusa Basin Drain.

#### III. Personnel

This project will be conducted by the Environmental Hazards Assessment Program (EHAP) under the general direction of Roger Sava, Senior Environmental Research Scientist (Supervisor). Key personnel are listed below:

Project Leader: Kevin Bennett

Field Coordinator: Nan Singhasemanon

Senior Scientist: Lisa Ross Data Analysis: Rosie Gallavan

Quality Assurance/Control: Nancy Miller Agency and Public Contact: Marshall Lee

Questions concerning this monitoring project should be directed to Marshall Lee at (916) 324-4100.

#### IV. Study Plan

Rice pesticides are monitored in the Colusa Basin Drain because it is a major agricultural drain discharging to the Sacramento River. CBD5 represents a culmination of most of the drainage from rice growing regions west of the Sacramento River. Data from previous studies (Lee 1994b, Lee and Gorder 1993 & 1992) have shown that significant rice pesticide concentrations in the Sacramento Valley are consistently found at CBD5. Water flowing past CBD5 represents a large percentage of rice field effluent for the Sacramento Valley, and this site has historically been used to monitor pesticide residues for the Rice Pesticides Monitoring Program. CBD5 was chosen as the sole monitoring site for 1995 because samples collected at this site have historically yielded the highest pesticide detections when compared to the other sites; the assumption being that if water quality performance goals are met at CBD5, they will be met elsewhere in the region.

The monitoring program will begin with background sampling in mid-April. Surface water sampling and water quality measurements will be performed twice weekly for a period of approximately ten weeks following initial field flooding. The predicted sampling schedule is presented below:

DATE	SITE (CBD5)		
Background (2 to 3 weeks prior)	<u>Day  </u> I <sup>a</sup> + biotoxicity	<u>Day 2</u> Not sampled	
Week 1	1	11 <sub>p</sub>	
2 *	Ĭ	Ħ	
3	1	11	
4	I	П	
5	I	П	
6	1	11	
7	I	11	
8	Ī	IIIc	
9	Ī	Ш	
10	1	111	

a) Schedule I: molinate, thiobencarb, carbofuran, methyl parathion and malathion + quality control set for all chemicals.

#### Estimated number of samples:

5 6 7	3 (1) 3 (1)	3 (1) 3 (1)	3 (1) 3 (1)	3 (1) 3 (1)	1
7	3 (1)	3 (1)	3 (1)	3 (1)	1
8	3 (1)	3 (1)	3 (1)	3 (1)	
9	3 (1)	3 (1)	3 (1)	3 (1)	0
10	3 (1)	3 (1)	3 (1)	3 (1)	
TOTALS	32 (11)	32 (11)	32 (11)	32 (11)	8

<sup>†)</sup> Methyl parathion and malathion are analyzed from a single sample.

Total Chemical Analyses = 128 samples
Biotoxicity (1 sample/wk x 8 wks) = 8 samples

Total = 136 samples

b) Schedule II: molinate, thiobencarb, carbofuran, methyl parathion and malathion + biotoxicity.

c) Schedule III: schedule I less quality control set.

<sup>‡)</sup> Numbers in parentheses indicate the number of samples taken for quality control under schedule I.

The biotoxicity samples and backups will be collected as part of the primary volume of water. Two un-acidified and acidified backup samples each will be collected and stored. All backups will be held in storage (4°C) until the initial data analysis is complete.

Water pH, temperature and dissolved oxygen will be measured *in situ*, at each site, during individual sampling periods.

### V. Sampling Methods

A cross-sectional water sample will be collected using the equal-width-increment sampling method (Edwards and Glysson 1988) which requires equal spacing of a number of sampling points across the drain based on its width and flow. This method utilizes a depth-integrated sampler (D-77) with a 3-liter Teflon<sup>®</sup> bottle and nozzle, nylon rope and stainless steel buckets as its sampling components. As the cross-sectional sampling proceeds, the sample will be composited temporarily in a stainless steel bucket until the appropriate volume of water has been collected. Then using a 10-port splitter (Geotech, model Dekaport), the water sample will be split into amber glass bottles and sealed with Teflon<sup>®</sup>-lined lids. Samples to be analyzed for carbofuran, methyl parathion and malathion will be acidified on site with 3N HCl to a pH between 3.0 and 3.5 for increased sample stability during storage. All samples will be stored on wet or blue ice (4 °C) until delivered to the laboratory for analyses.

Every attempt will be made to avoid both disturbing the bottom of the agricultural drain and sampling areas of the drain with no observable flow. As standard operating procedure, all sampling personnel will wear rubber gloves during sampling and if contamination is suspected, the gloves will be replaced.

Water temperature and pH will be measured with a Sentron pH/temperature meter (model 1001), and dissolved oxygen will be measured with a YSI (Yellow Springs Instrument) dissolved oxygen meter (model 57). Flow rates for CBD5 are available from a nearby gauging station and will be used to predict the mass loading of the five pesticides in the Colusa Basin Drain.

#### VI. Chemical Analysis and Biotoxicity

Chemical analysis for molinate and thiobencarb will be performed by Zeneca Agricultural Products and Valent USA respectively. FMC Corporation will perform the chemical analysis for carbofuran, and the California Department of Food and Agriculture (CDFA) Laboratory Services will perform the analysis on both methyl parathion and malathion. The reporting limit (RL) will be used to measure the lowest

concentration of analyte that the method can detect reliably in a matrix blank. The reporting limits for the monitoring program are listed below:

	$\mu y/I$
Molinate (Zeneca) -	1.0
Thiobencarb (Valent) -	0.5
Carbofuran (FMC) -	0.4
Methyl parathion (CDFA) -	0.1
Malathion (CDFA) -	0.1

These RLs may be lowered pending continuing laboratory contract negotiations. Chemical analytical methods will be provided in the final report.

CDFG's Aquatic Toxicology Laboratory (ATL) will determine toxicity using a 96-hour bio-assay with cladocerans. Percent survival of test organisms in undiluted sample water will follow current U.S. Environmental Protection Agency guidelines.

#### VII. <u>Ouality Assurance/Control</u>

As an inter-laboratory quality control measure, a minimum of 10% of the samples collected will be analyzed by CDFA for molinate, thiobencarb and carbofuran to verify results by Zeneca, Valent and FMC. Also, a minimum of 10% of the samples collected will be analyzed for methyl parathion and malathion by ALTA Analytical laboratory. Rinse blanks, blind matrix spikes and blanks will be submitted throughout the study under the auspices of the Quality Assurance Officer as continuing quality control. Details of EHAP's laboratory projection plan are available upon request and will be included in the final report.

#### VIII. Time Table

This study will be conducted at the start of the 1995 rice pesticide application season which typically begins during the month of April or May and will consist of the following:

Field Sampling - April through July 1995 Chemical and Toxicity Analysis - May through August 1995 Preliminary Report - September 1995 Final Report - November 1995

#### IX. References

California Department of Health Services. 1987. Proposed Maximum Contaminant Level, Thiobencarb (Bolero<sup>k</sup>). Hazard Evaluation Section, Berkeley.

Edwards, T.K. and D.G. Glysson. 1988. Field methods for measurement of fluvial sediment: U.S. Geological Survey Open-File Report 86-531. p. 61-64.

Finlayson, B.J., J.L. Nelson and T.L. Lew. 1982. Colusa Basin drain and reclamation slough monitoring studies, 1980 and 1981. California Department of Fish and Game, Environmental Services Branch, Administrative Report No. 82-3.

Lee, J.M. 1994. Personal communication between J.M. Lee and K.P. Bennett. California Department of Pesticide Regulation, Environmental Monitoring and Pest Management. September 8, 1994.

Lee, J.M. 1994b. Information on Rice Pesticides Submitted to the Central Valley Regional Water Quality Control Board. Memorandum to William H. Crooks, Executive Officer, California Regional Water Quality Control Board, Central Valley Region. California Department of Pesticide Regulation, Pest Management Assessment Program. March 8, 1994.

Lee, J.M. and N. Gorder. 1993. Information on Rice Pesticides Submitted to the Central Valley Regional Water Quality Control Board. Memorandum to William H. Crooks, Executive Officer, California Regional Water Quality Control Board, Central Valley Region. California Department of Pesticide Regulation, Pest Management Assessment Program. January 29, 1993.

Lee, J.M. and N. Gorder. 1992. Information on Rice Pesticides Submitted to the Central Valley Regional Water Quality Control Board. Memorandum to William H. Crooks, Executive Officer, California Regional Water Quality Control Board, Central Valley Region. California Department of Pesticide Regulation, Pest Management Assessment Program. February, 1992.

# Appendix E

APPENDIX E

### Memorandum

Roger Sava
Senior Environmental Research
Scientist Supervisor
1020 N Street, Room 161
Sacramento, California 95814-5624

November 22, 1995

Place :

Department of Pesticide Regulation - 1020 N Street, Room 161
Sacramento, California 95814-5624

Subject TOXICITY MONITORING IN RICE RECIRCULATING SYSTEMS

#### Scope of this Memorandum

The scope of this memorandum is to provide results from the Toxicity Monitoring in Rice Recirculating Systems Study. This memorandum does not include any interpretation of the data, which will be provided in the final report.

#### Background

In 1993 the Central Valley Regional Water Quality Control Board (CVRWQCB) monitored emergency water releases from rice fields (CVRWQCB 1993) 6 to 17 days after molinate and 14 to 41 days after carbofuran applications. Water samples from fields treated with both pesticides were all toxic to Ceriodaphnia dubia in toxicity tests. The results generated concern about toxicity in drainage canals of recirculating systems receiving such runoff.

Water releases from rice fields treated with carbofuran and molinate are allowed after a 28-day post-application hold. Prior to 1994, emergency releases were permitted 6 days after molinate and carbofuran applications. Beginning in 1994 emergency releases were permitted from molinate treated fields only when water was held for at least 11 days, and then only if the 28 day holding time following a carbofuran application had lapsed. In contrast, water from rice fields in recirculating irrigation systems may be released 8 days after application of both pesticides. Results from the CVRWQCB toxicity test infer that water in recirculating systems may be toxic to aquatic life. Therefore, this study was conducted to monitor water in recirculating systems for toxicity using Ceriodaphnia dubia as the test species.



RNAME

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#### Site Selection

Six rice fields were selected in Reclamation District no.108 (RD108), a multi-farm recirculating irrigation system in Colusa and Yolo counties. The selected fields were located in Colusa county, in the northern half of RD108. All fields used a post-flood "Leathers" or "Pin Point" method of carbofuran application to the checks and borders. The Leathers method is a post-flood application where the rice field is flooded, seeded, then the water level is lowered and carbofuran applied. The field is then reflooded and the water held for a minimum of 8 days. However, molinate is usually applied during the required 8 day carbofuran hold, and thus water cannot be released until at least 8 days after the molinate application.

#### Sampling Methods

The grower-cooperators were asked to release water at the earliest date that permit conditions allowed. Two replicate samples were taken from each field at its discharge point within 4-hours of the initiation of water release, background samples were collected at field irrigation inlets during the reflooding after the carbofuran applications. Two of the six field's discharge was sampled as it traveled through the drainage canals of the recirculating system. Water samples were collected in the drainage canal below the confluence of all subsequent canal outflows.

The discharge and background inlet water was collected as a grab sample, this water was assumed well mixed. Canal samples were collected using a hand held water sampler and the equal-width increment, depth integration method (Guy and Norman 1970). Flow rates and velocities at each canal sampling site were measured to determine appropriate sampling intervals, ensuring that the same parcel of water is monitored throughout the system.

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Each sample consisted of eleven liters of water. Samples were split using a Geotech® Dekaport splitter into ten 1-liter amber glass bottles with Teflon® lined caps and one 1-liter polypropylene bottle. All samples were split on the day of collection and shipped on wet ice or refrigerated at 4°C until analyzed.

#### Toxicity Testing and Chemical Analysis

Five 1-liter samples were delivered to the California Department of Fish and Game's Aquatic Toxicity Laboratory (ATL) for toxicity testing. ATL initiated 96-hr toxicity test using Ceriodaphnia dubia within 30 hours of sample collection. Toxicity Identification Evaluation (TIE) was performed on the most toxic samples. ATL also received a 1-liter (polypropylene bottle) sample for copper analysis.

Three 1-liter samples were analyzed by the California Department of Food and Agriculture Chemistry Laboratory. Chemical analysis included molinate, thiobencarb, carbofuran, methyl parathion, and malathion. Immediately after splitting samples analyzed for carbofuran, methyl parathion, and malathion were acidified with 3N HCl to pH3 to increase storage stability (Miller 1991). The quality control split samples were analyzed by Alta Analytical Laboratory for carbofuran, methyl parathion, and malathion, and APPL Laboratory for molinate and thiobencarb.

#### Field Measurements

Water pH and temperature were measured with a Sentron (model 1001) pH/temperature meter. EC was measured with an Orion salinity-conductivity-temperature meter (model 140), and DO with a YSI dissolved oxygen meter (model 57). Ammonia was measured using an ammonia-nitrogen test kit made by CHEMetes (model AN-10). A Price meter, type AA, was used for flow measurements in the drainage canals.

#### Results

Toxicity test on water from the outlets of fields B1 and D2 had survival rates for *Ceriodaphnia dubia* of 0 and 25%, respectively (Table 1). These fields had very low water levels at the time of sampling and normally would not have discharged water, however, water was released at our request. The low water level may have attributed to the higher pesticide concentrations in the outlet water which affected the mortality rate in these samples. The survival rates from the remaining outlet sites ranged from 65 to 100%.

The inlet and canal samples had survival rates of 70 to 100% with the exception of the canal sample at the outlet of field B1, which had a 25% survival of Ceriodaphnia dubia (Table 2).

The outlet concentrations for the six fields ranged from .87 to 10.1 ppb for carbofuran, no detectable amount to 194 and 252 ppb for thiobencarb and molinate respectively. Molinate was not applied to field D1, and fields A1, A2, A3, and B1 did not receive thiobencarb applications. Carbofuran was not detected in any inlet samples, while the concentrations of molinate and thiobencarb were below 8 ppb. The canal sample concentrations ranged from no detectable amount to 2.74 and 15.9 ppb for carbofuran and thiobencarb respectively, and 12.7 to 144 ppb for molinate.

Methyl parathion and malathion were not detected in any samples. Results from TIE and copper analysis have not been received from the laboratory, but will be included in the final report.

Table 1. Pesticide concentrations and toxicity results of field inlet and outlet water. Values in parenthesis are the number of days after pesticide application when water samples were collected.

	Toxicity,  * Survival (control/sample)		Carbofuran ppb		Molinate ppb		Thiobencarb ppb	
	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet
Field Al	95/75	95/65	nd (2)	2.13(14)	0.1	107(10)	1	0.1(na)
Field A2	95/100	100/95	nd (2)	0.93(14)	2.18	166(9)	nd	nd(na)
Field A3	100/100	95/100	nd (0)	0.87(12)	nd	215(9)	nd	nd(na)
Field Bl	100/100	95/0	nd (3)	10.1(18)	7.36	252 (9)	6.97	0.3 (na)
Field D1	100/95	100/80	nd (2)	1.5(15)	nd	nd (na)	nd	72.2(12)
Field D2	95/100	100/25	nd (3 )	1.37(16)	nd	164 (10)	4.12	194 (12)

nd = Not Detected, see appendix for minimum detection limits.

na = Chemical not applied.

Table 2. Pesticide concentrations and toxicity results of canal water from two fields. Values in parenthesis are the number of days after pesticide application when water samples were collected.

		Toxicity,  Survival (control/sample)	Carbofuran ppb	Molinate ppb	Thiobencarb ppb
Field A3	Outlet	95 / 100	0.873 (12)	215 (9)	nd
Canal	0*	95 / 100	0.498 (12)	130 (9)	nd
	1	95 / 70	0.52 (12)	142 (9)	nd
	2	95 / 95	0.343 (12)	57 (9	nd
	3	95 / 90	0.452 (12)	144 (9)	nd
	4	95 / 100	0.269 (12)	32.8 (9)	1.64
	5	95 / 100	0.437 (12)	107 (9)	1.06
	6	95 / 100	0.114 (12)	34.6 (9)	15.9
Field Bl	Outlet	95 / 0	10.1 (18)	252 (9)	0.3
Canal '	Upstream	95 / 100	nd	0.72 (9)	nd
	0*	95 / 25	2.74 (18)	63.9 (9)	nd
	1	100 / 100	0.231 (18)	15.6 (9)	nd
	2	100 / 100	nd (18)	12.7 (9)	0.47
	3	100 / 80	0.359 (18)	22.1 (9)	5.72
	4	100 / 95	nd (18)	19.1 (9)	5.52
	5	100 / 85	0.15 (18)	54.7 (9)	7.15

nd = Not Detected. Refer to appendix for minimum detection limits.
\* 0 = Canal sampled at field discharge, 1 thru 6 are subsequent downstream samples.

#### IX. References

California Regional Water Quality Control Board - Central Valley Region, 1993. Molinate Concentrations in Rice Field Discharges, 1993. Memorandum from Rudy Schnagl and Wendy Wyels to Marshall Lee. August 6, 1993.

Guy, H.P. and V.W. Norman. 1970. Field methods for measurement of fluvial sediment. <u>In:</u> Techniques of Water-Resources Investigations of the United States Geological Survey, Book 3, Chapter C2, 59p.

Miller, Nancy. 1991. Study X87 - Storage Stability Study for Carbofuran. California Department of Food and Agriculture Chemistry Laboratory - in house study.

Dan Li

Dave Kim
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# Appendix F

APPENDIX F

## STATE OF CALIFORNIA DEPARTMENT OF FISH AND GAME

#### PESTICIDE LABORATORY REPORT

1701 Nimbus Road, Suite F Rancho Cordova, California 95670

Lab No:F	21751	Date Received: 04/14/95 05/23/95 06/06/95	05/16/95 05/30/95 06/13/95
		06/20/95	06/27/95
E.P. No	<del></del>	Sample:	
Го:	Mr. Brian Finlayson, ES IV	Report Date:	08/01/95
ADDRESS:	Pesticide Investigations Unit 1701 Nimbus Road, Suite F		

#### Remarks:

Water samples were collected weekly by Department of Pesticide Regulation staff from the Colusa Basin Drain (CBD) Site CBD5 from April 14 to June 27, 1995 during a routine pesticide and toxicity monitoring study. Samples were analyzed for pesticides by DPR staff. Water quality and acute toxicity were determined by DFG staff. Neonate cladocerans (<24-h old Ceriodaphnia dubia) were exposed to undiluted water samples for 96 hours. The control water was prepared by diluting commercial spring or mineral water with high-purity deionized water. The toxicity tests were conducted as static tests with renewal of the solution after 48 hours.

Rancho Cordova, CA 95670

#### RESULTS OF EXAMINATION

#### Water Quality Parameters

Water samples were analyzed for specific conductivity, total alkalinity, total hardness, and total ammonia (Table 1). The water quality data did not indicate any specific condition considered deleterious to the test organism.

#### Pesticide Residues

Water samples were analyzed for five pesticides; molinate, thiobencarb, malathion, methyl parathion, and carbofuran. Preliminary pesticide residues were reported by Gorder (1995) and Bennett (1995; Table 2). All five pesticides were found in detectable concentrations during the study period. The herbicides molinate and thiobencarb were found persistently in water samples taken after April 14, 1995. The insecticide carbofuran was detected in four samples during the study period. Detectable concentrations of the insecticides malathion and methyl parathion were only found in the mid-May collections.

#### Toxicity Test Results

The undiluted samples from CBD5 showed no statistically significant mortality in the C. dubia tests, except for the sample collected on May 30, 1995 (Table 3). Percent survival was 55 % after exposure to water collected. Mortality of cladocerans on May 30, 1995, did not appear to be caused by pesticide toxicity; concentrations of all pesticides (Table 2) were less than 5 % of their respective  $LC_{50}$  values (Table 4). The concentrations of thiobencarb (1.2  $\mu$ g/L) and molinate (19  $\mu$ g/L) detected on this date were well below the reported 48-h  $LC_{50}$  values of 510 and 9,130  $\mu$ g/L, respectively (Table 4). Toxicity identification evaluation procedures should be used in future tests to identify the cause(s) of toxicity in these samples.

PESTICIDE INVESTIGATIONS UNIT ENVIRONMENTAL SERVICES DIVISION

By B. Fujimura

Robert Fujimura

Environmental Specialist III

cc: John Sanders

Department of Pesticide Regulation
Sacramento, California

#### References Cited

- Bennett, K. 1995. Fax transmission to Bob Fujimura. CBD5 -preliminary results. Department of Pesticide Regulation, Sacramento, CA.
- Gorder, N. 1995. Fax transmission to Brian Finlayson. 1995 rice monitoring data. Department of Pesticide Regulation, Sacramento, CA.
- Norberg-King, T., E. Durhan, G. Ankley, and E. Robert. 1991. Application of toxicity identification evaluation procedures to the ambient waters of the Colusa Basin Drain, California. Environmental Toxicology and Chemistry, 10:891-900.

Mr. Brian Finlayson P-1751 Page 4

Table 1. Water quality data for Colusa Basin Drain (CBD5) samples collected from April 14, 1995 to June 27, 1995.

Collection Date	Total Alkalinity (mg/L CaCO <sub>1</sub> )	Total Hardness (mg/L CaCO <sub>1</sub> )	Specific Conductivity (µS/cm)	Total Ammonia (mg/L N)
4/14/95	218	238	687	0.130
5/16/95	140	142	427	0.051
5/23/95	180	180	575	0.067
5/30/95	190	203	660	0.056
6/6/95	182	194	667	<0.050
6/13/95	189	201	766	0.054
6/20/95	158	150	469	<0.050
6/27/95	224	238	963	0.083

Concentrations ( $\mu$ g/L) of five pesticides in water from the Colusa Basin Drain at CBD5 in 1995. Data is preliminary and subject to revision (Gorder 1995; Bennett 1995). Only the results of the Table 2. primary water sample are presented here. Results in brackets are from the backup sample.

ollection	Pesticide Concentrations					
Date	Molinate	Thiobencarb	Malathion	Methyl <u>Parathion</u>	Carbofurar	
4/14/94	ИD	ND	ND .	ND	ND	
5/16/95	9.3	ND	<b>≺ 1.03</b>	<b>+ 0.08</b>	÷ 0.70	
5/23/95	[15.4]	[0.8]	ND	0.06	0.67	
5/30/95	19	1.2	ND	ND	ND	
6/6/95	16.5	1.3	ND	ИD	0.45	
6/13/95	10.7	1.7	ND	ND	0.39	
6/20/95	10.4	0.5	ND	ND	ND	
6/27/95	8.0	0.5	ND	ND	ŊD	

\* re.1 17 GRA palient of a factory por 10 1:

20 regaments total

Survival of Ceriodaphnia dubia neonates (<24-h old) to Table 3. undiluted water samples from the Colusa Basin Drain at CBD5 in 1995. Asterisks indicate survival significantly less than the control group (P < 0.05).

Collection Date	Percent	Commone	
	Clado	Comments	
	<u>Control</u>	Sample	
4/14/95 4/14/95	100 100	100	dina 1
5/16/95	100	95	duplicate test
5/23/95	100	85	
5/30/95	95	55*	
6/6/95 6/6/95	95 100	100 95	dom's
5/13/95	100	100	duplicate test
/20/95	100	100	
/27/95 /27/95	95 90	95 95	duplicate test

Acute toxicity (48-h LC<sub>50</sub> in  $\mu$ g/L) values for five pesticides for the cladoceran Ceriodaphnia dubia.

Chemical	ordeceian Ceriodaphnia dubia.
Second Cal	48-h LC <sub>50</sub> Value
Molinate	
Thiobencarb	9,130
•	510 <sup>b</sup>
Malathion	1.4 <sup>b</sup>
Methyl Parathion	<b>1.4</b>
	2.6 <sup>b</sup>
Carbofuran	2.6
DFG unpublished data	
Norham Winn	

Norberg-King et al. 1991

# Appendix G

## CALIFORNIA DEPARTMENT OF PESTICIDE REGULATION Environmental Hazards Assessment Program (EHAP)

# Laboratory Project Plan for the 1995 Rice Pesticides Monitoring Program March 1, 1995

#### Organization and Responsibility

The EHAP project leader will be Kevin Bennett, Department of Pesticide Regulation. The EHAP project leader has the overall responsibility for all aspects of the field monitoring including: prepares and approves the protocol; approves the selection of QA officer, field coordinators and sampling crew; reviews EHAP's QA summaries; submits laboratory QA/QC plan and QA reports to the EHAP agency contact person; submits data generated in the study to the agency contact person.

Nancy Miller will be assigned EHAP QA officer, Department of Pesticide Regulation. Her duties include: prepares and approves the lab project plan; approves selection of sample custodian; reviews laboratory QA/QC plans and QA reports; meets or communicates with project leader, field coordinator and sample custodian to evaluate progress and resolve problems; conducts audits of laboratory; submits QA reports to EHAP project leader.

Marshall Lee will be the assigned agency contact person for the Department of Pesticide Regulation. His duties include the overall responsibility of agency communications concerning this monitoring project.

All laboratories shall assign one contact person to report all information including analytical data to the EHAP QA officer.

#### Protocol

The monitoring program shall follow the approved written EHAP protocol (Appendix 1). Changes to the protocol must be approved by the EHAP project leader.

#### **Quality Assurance Objectives**

Each laboratory shall determine a method detection limit (MDL), instrument detection limit (IDL) and a reporting limit (RL) for each analyte. Each laboratory shall also document their terms, definitions and procedures for determining MDL, IDL and RL in their approved analytical method.

#### Method Validation

For method validation each laboratory will perform 5 replicate matrix spikes at 3 different concentrations each ranging from the reporting limit to the highest anticipated field concentration level (Appendix 2).

The mean and standard deviation (s) values from the method validation will be used to set warning and control limits at +\- 2s and +\- 3s, respectively. Each laboratory will also be required to provide a copy of their approved analytical method before analyzing any field samples.

#### Continuing Quality Control

Accuracy is defined as a determination of how close the measurement is to the true value and is often described as percent recovery. Accuracy is to be expressed as Percent Recovery (%). All calculated values for accuracy shall be presented with the analytical results. The equation for calculating Percent Recovery is as follows:

Accuracy will be assessed by requiring each laboratory to analyze two matrix spike samples per analyte for each extraction set of up to twelve field samples (Appendix 3).

Accuracy control charts will be plotted by EHAP for each chemical and method and for each control sample matrix. The warning and control limits are established as listed in the method validation section. If any continuing quality control spike recovery is not within the limits of these criteria, the following is required:

1. A check shall be made to be sure there are no errors in calculations, surrogate solutions, and internal standards. A check shall also be made on instrument performance.

- 2. All affected data shall be recalculated and/or the extract shall be reanalyzed if any of the above checks reveal a problem.
- 3. All affected samples shall be reextracted and reanalyzed if none of the above is identified as a problem.
- 4. All analytical data shall be flagged as "suspect" if the accuracy still does not fall within the limits of the above criteria. The laboratory QA officer shall notify the EHAP QA officer within 1 working day after discovery of "suspect" data.
- 5. If an unacceptable value cannot be corrected, additional samples may be analyzed to determine the validity of the original sample results.

The calibration curve should be prepared such that one standard is at the reporting limit and one is higher than the highest expected amount. If after initially shooting the sample extract the concentration of the analyte falls outside the calibration range, the sample should be diluted so it falls within the calibration range. Each laboratory shall document in the analytical method their calibration procedures. As an interlaboratory quality control check a minimum of ten percent of the total samples collected will be analyzed by a second laboratory for verification. CDFA laboratory will analyze split samples for molinate, thiobencarb and carbofuran. ALTA Analytical laboratory will analyze splits for methyl parathion and malathion.

In addition, two rinse blanks per week will be submitted to check for potential field contamination while blind matrix spike samples will be routinely submitted to each laboratory to check for accuracy.

Background surface water will be provided by EHAP to the laboratories and used for control and fortification samples.

Audits of the field sampling and lab analysis may be conducted.

#### Reporting

Results of field sample and continuing quality control analyses shall be reported to the EHAP QA officer within 21 days of the date samples are received at each laboratory. Each laboratory shall submit legible, organized reports which contain analytical results of all samples received from EHAP. Analytical results are to be expressed as ug/L to three significant figures for all samples. Positive matrix blank results shall be reported. Do not correct field sample results for background levels. Indicate if the results have been adjusted for spike recoveries. Each laboratory shall document in the analytical method their procedures for reporting sample results including number rounding procedures. The report shall evaluate the quality of the individual sample data, based on the method validation analyses. The reports shall include the following:

- 1. Chain of custody (COC) forms; all analytical results are to be reported on the COC, including the name of the person extracting and analyzing the sample, date of extraction and the date of analysis for each sample
- 2. Records of any quality assurance problems and questions pertaining to the samples analyzed
- 3. Calculations of accuracy
- 4. Reporting Limit (RL); for those samples that contain no detectable amount, write "ND" and indicate the RL
- 5. Case narrative, if the data requires it

In addition, the laboratory shall be prepared to provide to the EHAP QA officer all sample custody paperwork, records of times and dates of analyses, and raw data pertaining to both the analyses and the quality control checks within 10 working days after the information is requested.

#### **Archives**

All backup samples and sample extracts shall be stored frozen or refrigerated until the study director authorizes their disposal.

All raw data, including chromatograms, memoranda, notes, worksheets, and calculations that are necessary for the reconstruction and evaluation of the study shall be archived at each respective laboratory for at least three years.

#### **APPROVALS**

Kevin Bennett EHAP Project Leader	Mancy Miller EHAP Quality Assurance Officer
Catherine Cooper Calif. Dep. Food & Ag. Laboratory	Sharon Pierson ALTA Analytical Laboratory
Daniel Killingsworth Zeneca Ag Products, Inc.	Alan Smith FMC Laboratory
Charles Green Valent Dublin Laboratory	

#### Appendix 2

### 1995 Rice Pesticide Analytical Method Validation Study

Using background surface water, each laboratory will generate and analyze the following matrix spikes in order to determine precision and accuracy for each analytical method. The method validation phase shall be completed by **March 30, 1995**. All method validation results including the method write-up will be submitted to the EHAP QA officer before analyzing any field monitoring samples.

Methyl Parathion	PRIMARY LAB CDFA	SECONDARY LAB ALTA
5 reps each @	2 X RL 5 X RL 10 X RL	2 X RL 5 X RL 10 X RL
Malathion	CDFA	ALTA
5 reps each @	2 X RL 5 X RL 10 X RL	2 X RL 5 X RL 10 X RL
Molinate	Zeneca	CDFA
5 reps each @	1.0 ppb 10.0 ppb 20.0 ppb	2 X RL 10 X RL 100 X RL
Thiobencarb	<u>Valent</u>	CDFA
5 reps each @	0.5 ppb 5.0 ppb 10.0 ppb	2 X RL 10 X RL 100 X RL
Carbofuran	FMC	CDFA
5 reps each @	0.4 ppb 2.0 ppb 4.0 ppb	2 X RL 5 X RL 10 X RL

#### Appendix 3

#### 1995 Rice Pesticide Continuing Quality Control Procedures

Using background surface water, each laboratory will generate and analyze the following blank matrix and matrix spikes with each extraction set in order to determine accuracy over the duration of the study. All continuing quality control data will be submitted to the EHAP QA officer with each extraction set. Make sure individual field sample numbers are clearly identified with each set.

Methyl Parathion and Malathion		
Metry: Paratition and malatition	CDFA	<u>ALTA</u>
1 blank and 2 matrix spikes	5 X RL	5 X RL
Molinate		
	<u>Zeneca</u>	<u>CDFA</u>
1 blank and 2 matrix spikes	5.0 ppb	10 X RL
Thiobencarb		
	<u>Valent</u>	<u>CDFA</u>
1 blank and 2 matrix spikes	1.0 ppb	10 X RL
Carbofuran		
	<u>FMC</u>	<u>CDFA</u>
1 blank and 2 matrix spikes	1.0 ppb	5 X RL

## Performance Goals for the 1995 Rice Pesticide Study

Methyl Parathion 0.13 ppb

Malathion 0.1 ppb

Molinate 10 ppb

Thiobencarb 1.5 ppb

Carbofuran 0.4 ppb